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THE UNIVERSITY OF ALBERTA

ELECTRONIC ENERGY BAND CALCULATIONS

by

Robert S. Julius

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES  
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE  
OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

EDMONTON, ALBERTA  
SEPTEMBER, 1962



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Robert E. Wilson

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FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled ELECTRONIC ENERGY BAND CALCULATIONS, submitted by Robert S. Julius, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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## ABSTRACT

This thesis is concerned with the one-electron approximation to the problem of finding solutions of the Schrodinger equation for the particles in a crystalline solid.

The implications of the rotational and translational invariance of the Hamiltonian in the one-electron equation are reviewed. We see how the translational invariance leads to the Bloch form of the wave function and to the natural introduction of reciprocal space and Brillouin zones. We see also that the possible symmetries of the wave function are dictated by the rotational invariance of the Hamiltonian.

The anomalous skin effect, cyclotron resonance, and the de Haas van Alphen effect are reviewed briefly. We consider next some of the more standard methods for obtaining approximate solutions to the one-electron equation. These methods include the Wigner-Seitz cellular method, the Tight Binding procedure, and several variations of the Plane Wave methods.

Three new procedures are then developed for obtaining approximate solutions to the one-electron equation. The first of these is a cellular method which provides conveniently  $E(\bar{k})$  for those special values of  $\bar{k}$  which are highly symmetric in the first Brillouin zone. Next we develop a determinantal procedure which produces an implicit approximation to the entire  $(E, \bar{k})$  relation. Finally, an interpolation procedure based upon the other two new methods is devised.

The new methods are applied in some detail to the one dimensional empty lattice and the Kronig-Penny model, with





very satisfactory results in both cases. The methods were then applied to a plane hexagonal lattice with two distinct types of potential, and the results are encouraging. Application of the new cellular method to a face centered cubic lattice proceeded until the capacity of the available computing facilities was exceeded. Some of the possible directions for future work are indicated.





## ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the assistance and encouragement of my supervisor, Dr. D. D. Betts, who gave freely of his time during the course of this research.

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## CHAPTER I

### INTRODUCTION

Since 1940 and earlier, physicists have been concerned with methods of obtaining approximations to the solutions of the Schrodinger equation for the particles in a crystalline solid. It is normally assumed that the atomic nuclei are at rest at fixed positions in the lattice, and there remains, then, an equation involving the wave functions of many electrons, the interaction of the ion cores upon these electrons, and the mutual interactions between the electrons. This many-electron equation has not been solved analytically, and a strictly numerical approach does not appear promising.

The one-electron approximation to the problem assumes that each electron is adequately described by Schrodinger's equation with a potential energy term due in part to the fixed ion cores, and in part to some average potential due to the other electrons. The ion core portion of the potential that is used may or may not attempt to include the effect of the inner, tightly bound electrons. The one-electron approximation gives rise to two problems: the setting up of the appropriate Hamiltonian for the system, and then the solution of the resultant equation.

Except for a brief discussion of the ion core portion of the potential in Chapter VII, we concern ourselves with methods of finding approximate solutions to Schrodinger's equation, given the potential. In Chapter II we see how the translational invariance of the Hamiltonian (assuming an infinite lattice) leads to the Bloch form of the wave function and to the natural introduction of reciprocal space and Brillouin

# THE FUTURE

The future is a concept that has fascinated humanity for centuries. It is a time when the unknown meets the known, where dreams and aspirations take shape. The future is not just a distant point in time; it is a state of mind, a way of seeing the world. It is the potential for growth, change, and progress. The future is what we create through our actions and decisions in the present. It is the result of our choices, our efforts, and our vision. The future is a canvas upon which we paint our hopes and dreams. It is a place where the impossible becomes possible, where the unimaginable becomes reality. The future is a journey, a path that leads us from the present to the unknown. It is a journey of discovery, of exploration, and of growth. The future is a time when we can make a difference, when we can leave a legacy, when we can create a better world for ourselves and for future generations. The future is a time when we can achieve our dreams, when we can reach our goals, when we can make our mark on the world. The future is a time when we can be the change we want to see in the world. The future is a time when we can be the best version of ourselves. The future is a time when we can be the difference. The future is a time when we can be the future.



zones. Following Mott and Jones (1958) we then see that the energy  $E$  exhibits a band structure as a function of  $\bar{k}$  where  $\psi = e^{i\bar{k} \cdot \bar{r}} u_{\bar{k}}(\bar{r})$ , and where  $u_{\bar{k}}(\bar{r})$  has the translational invariance of the potential. We then discuss the symmetry of the wave function which results from the rotational invariance of the Hamiltonian, and finally the symmetry of  $E(\bar{k})$  and the nature of surfaces of constant energy is investigated.

To varying degrees of approximation, Chapter III is concerned with the theoretical bases for three phenomena which are more or less amenable to experiment, and which enable one to gain some knowledge of the geometrical characteristics of the Fermi surface of a metal. The three phenomena considered are the anomalous skin effect, cyclotron resonance, and the de Haas-van Alphen effect.

In Chapter IV some of the more widely used methods for obtaining approximate solutions to the one-electron formulation of the problem are reviewed. The methods considered are the Wigner-Seitz cellular method and some of its variations, several Tight Binding procedures, and several variations of the Plane Wave methods.

After considering a matrix equation which is equivalent to the Schrodinger equation for the problem, the standard variational procedure is discussed in Chapter V. Following this, three new methods for obtaining approximate solutions are developed: the method of Restricted Cellular Basis Functions, a determinantal method, and an interpolation procedure based upon the previous two new methods.

Chapter VI comprises several applications of the new methods which illustrate their use, and also their rates of convergence in some special cases. Chapter VII gives a brief review and comparison of some of the methods considered.



## CHAPTER II

### THE THEORY OF ELECTRONIC ENERGY BANDS

In this chapter we consider the nature of solutions to the Schrodinger equation

$$H\psi = E\psi, \quad (2.1)$$

where  $H$  is of the form

$$H = -\nabla^2 + V(\vec{r}) \quad (2.2)$$

and where  $V$  is periodic. That is

$$V(\vec{r} + A\vec{n}) = V(\vec{r}) \quad (2.3)$$

where the  $i$ 'th column vector of the matrix  $A$  is  $\vec{a}_i$  and the elements of the column vector  $\vec{n}$  are integers. For the sake of convenience we will treat  $\vec{r}$  as a vector in three dimensional space, though all of the following material holds with but little modification in one and two dimensional spaces. Much of the material in this chapter is merely a reorganization of work which has appeared in many texts and papers. The main references have been Jones (1960), Mott and Jones (1958), Lomont (1959) and Wigner (1959). The notation, of course, has been made consistent.

Since  $\nabla^2$  is independent of translations and orientation, and since  $V(\vec{r})$  is periodic, the Hamiltonian  $H$  is invariant under two types of operation: translations by any integer linear combination of the basis vectors  $\vec{a}_i$  of the lattice, and by any rotation and/or reflection which leaves the lattice (i.e.  $V$ ) unchanged.

#### Bloch Wave Functions

Let us consider first the implications of the translational



# THE HISTORY OF THE UNITED STATES

The history of the United States is a story of growth, struggle, and achievement. From the first settlers to the present day, the nation has evolved through various challenges and triumphs. The early years were marked by exploration and the establishment of colonies. The American Revolution led to the birth of a new nation, one that sought to define its own identity and values. The 19th century was a period of westward expansion and the struggle for slavery. The 20th century brought the challenges of industrialization, war, and social change. Today, the United States continues to shape the world and its future.

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invariance of  $H$ . We denote by  $g_{\bar{n}}$  that translation operator which maps  $f(\bar{r})$  into  $f(\bar{r} + A\bar{n})$ . That is

$$g_{\bar{n}}f(\bar{r}) \equiv f(\bar{r} + A\bar{n}). \quad (2.4)$$

Since

$$g_{\bar{m}}g_{\bar{n}}f(\bar{r}) = g_{\bar{m}}f(\bar{r} + A\bar{n}) = f(\bar{r} + A(\bar{n} + \bar{m})) = g_{\bar{n} + \bar{m}}f(\bar{r}), \quad (2.5)$$

the operations  $(g_{\bar{m}})$  clearly form a group  $G$  as  $\bar{m}$  runs through all integer vectors. The group  $G$  is abelian, since

$$g_{\bar{n} + \bar{m}} = g_{\bar{m} + \bar{n}}, \quad (2.6)$$

and  $H$  is invariant under the operations of this group; that is

$$g_{\bar{n}}Hf(\bar{r}) = Hg_{\bar{n}}f(\bar{r}). \quad (2.7)$$

Suppose now that  $\phi(\bar{r})$  is a solution to (2.1) for the particular value of the eigenvalue  $E = E'$ . That is, we assume that

$$H\phi(\bar{r}) = E'\phi(\bar{r}). \quad (2.8)$$

If we now operate on both sides of this equation by the translation operator  $g_{\bar{m}}$ , we find

$$g_{\bar{m}}H\phi(\bar{r}) = Hg_{\bar{m}}\phi(\bar{r}) = H\phi(\bar{r} + A\bar{m}); \quad (2.9)$$

and

$$g_{\bar{m}}E'\phi(\bar{r}) = E'\phi(\bar{r} + A\bar{m}). \quad (2.10)$$





That is

$$H\varphi(\bar{r}+A\bar{m}) = E'\varphi(\bar{r}+A\bar{m}). \quad (2.11)$$

$\varphi(\bar{r}+A\bar{m})$  then, is also a solution of (2.1), not necessarily distinct from  $\varphi(\bar{r})$ , corresponding to the eigenvalue  $E'$ . Then, given any solution  $\varphi(\bar{r})$  to (2.1), we can generate an infinity of solutions  $\varphi(\bar{r}+A\bar{n})$ , for all integer vectors  $\bar{n}$ , all of which correspond to the same eigenvalue. Let us now order the vectors  $\bar{n}$  in some fashion and label them  $\bar{n}_i$ , and define the row vector

$$\bar{\varphi}^T(\bar{r}) \equiv \left[ \dots, \varphi(\bar{r}+A\bar{n}_{-1}), \varphi(\bar{r}+A\bar{n}_0), \varphi(\bar{r}+A\bar{n}_1), \dots \right] \quad (2.12)$$

We now define the effect of operating on  $\bar{\varphi}(\bar{r})$  with  $g_{\bar{k}}$  to be

$$g_{\bar{k}}\bar{\varphi}^T(\bar{r}) \equiv [\dots, g_{\bar{k}}\varphi(\bar{r}+A\bar{n}_{-1}), g_{\bar{k}}\varphi(\bar{r}+A\bar{n}_0), g_{\bar{k}}\varphi(\bar{r}+A\bar{n}_1), \dots]. \quad (2.13)$$

But

$$\begin{aligned} g_{\bar{k}}\varphi(\bar{r}+A\bar{n}_i) &= \varphi(\bar{r}+A(\bar{k}+\bar{n}_i)) \\ &= \varphi(\bar{r}+A\bar{n}_j) \end{aligned} \quad (2.14)$$

for some permissible vector  $\bar{n}_j$ . The vector  $g_{\bar{k}}\bar{\varphi}$  is then a vector the components of which are merely a permutation of the components of  $\bar{\varphi}$  itself. We define

$$g_{\bar{k}}\bar{\varphi} \equiv \bar{\varphi}_{\bar{k}}, \quad (2.15)$$

and the  $m$ 'th component of  $\bar{\varphi}_{\bar{k}}$  is given by



$$[\bar{\varphi}_{\bar{k}}(\bar{r})]_m = g_{\bar{m}} g_{\bar{k}} \varphi(\bar{r}). \quad (2.16)$$

Consider now a set of infinite matrices  $G_{\bar{k}}$ , where each row of  $G_{\bar{k}}$  contains exactly one 1, and each column contains exactly one 1, and the remainder of the elements of  $G_{\bar{k}}$  are zero; that is, the  $(G_{\bar{k}})$  are a set of permutation matrices. Clearly, the elements of the column vector  $G_{\bar{k}} \bar{\varphi}(\bar{r})$  are again the elements of  $\bar{\varphi}$  in some permuted order; choose the  $G_{\bar{k}}$  such that

$$G_{\bar{k}} \bar{\varphi} = \bar{\varphi}_{\bar{k}} = g_{\bar{k}} \bar{\varphi}. \quad (2.17)$$

The set of matrices  $(G_{\bar{k}})$  obviously form a representation of the group  $G$ , and in fact, they form the so-called "Regular Representation" of  $G$ .

Now, since  $(G_{\bar{k}})$  is a representation of the group  $G$ , and since

$$(SG_{\bar{m}} S^{-1})(SG_{\bar{n}} S^{-1}) = SG_{\bar{m}} G_{\bar{n}} S^{-1}, \quad (2.18)$$

then the set  $(SG_{\bar{k}} S^{-1})$  for any non-singular  $S$  also forms a representation of  $G$ . Because  $G$  is Abelian, it can be shown that  $S$  may be chosen such that every member of the representation  $(SG_{\bar{k}} S^{-1})$  of  $G$  is diagonal.

We had chosen  $G_{\bar{k}}$  such that

$$G_{\bar{k}} \bar{\varphi}(\bar{r}) = \bar{\varphi}_{\bar{k}}(\bar{r}), \quad (2.17)$$

therefore

$$(SG_{\bar{k}} S^{-1})(S\bar{\varphi}(\bar{r})) = S\bar{\varphi}_{\bar{k}}(\bar{r}). \quad (2.19)$$

Let us define the matrices

$$J_{\bar{m}} = SG_{\bar{m}} S^{-1} \quad (2.20)$$



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and the vectors

$$\bar{\psi}_{\bar{m}}(\bar{r}) = S\bar{\phi}_{\bar{m}}(\bar{r}). \quad (2.21)$$

We note that since the  $J$ 's are diagonal, each set of numbers consisting of the  $n$ 'th diagonal element of all of the matrices  $J_{\bar{m}}$ , forms an irreducible representation of the group  $G$ .

Now,  $\phi(\bar{r})$  was chosen to be a solution to (2.1) corresponding to  $E=E'$ . If we say that  $g_{\bar{0}}$  is the unit element of  $G$ , then

$$\bar{\phi}_{\bar{0}}(\bar{r}) \equiv \bar{\phi}(\bar{r}), \quad (2.22)$$

and each component of  $\bar{\phi}_{\bar{0}}$  is also a solution corresponding to  $E'$ . and since the components of  $\bar{\phi}_{\bar{k}}$  are those of  $\bar{\phi}_{\bar{0}}$  in permuted order, each component of  $\bar{\phi}_{\bar{k}}$  is a solution corresponding to  $E'$ . But the components of  $\bar{\psi}_{\bar{k}}$  are merely linear combinations of those of  $\bar{\phi}_{\bar{k}}$ . In fact, from equation (2.21) we see that

$$[\bar{\psi}_{\bar{k}}]_m = \sum_t S_{mt} [\bar{\phi}_{\bar{k}}]_t. \quad (2.23)$$

That is, the components of  $\bar{\psi}_{\bar{k}}(\bar{r})$  are individually solutions to (2.1) corresponding to  $E = E'$ .

Now, from equations (2.19), (2.20), and (2.21) we have

$$J_{\bar{k}}\bar{\psi}_{\bar{0}} = \bar{\psi}_{\bar{k}}, \quad (2.24)$$

and since each  $J$  is diagonal

$$(J_{\bar{k}})_{mm} [\bar{\psi}_{\bar{0}}]_m = [\bar{\psi}_{\bar{k}}]_m. \quad (2.25)$$

But operating on  $\bar{\psi}_{\bar{0}}$  with  $J_{\bar{k}}$  is equivalent to operating on  $\bar{\psi}_{\bar{0}}$  with  $g_{\bar{k}}$ , since





$$\begin{aligned}
g_{\bar{k}} \bar{\psi}_{\bar{0}} &= g_{\bar{k}} S \bar{\phi}_{\bar{0}} = g_{\bar{k}} S \bar{\phi} \\
&= S g_{\bar{k}} \bar{\phi} = S \bar{\phi}_{\bar{k}} \\
&= \bar{\psi}_{\bar{k}}.
\end{aligned} \tag{2.26}$$

Therefore, equation (2.25) implies that

$$(J_{\bar{k}})_{mm} [\bar{\psi}_{\bar{0}}]_m = g_{\bar{k}} [\bar{\psi}_{\bar{0}}]_m. \tag{2.27}$$

Now,  $[\bar{\psi}_{\bar{0}}(\bar{r})]_m$  is a solution of  $H\psi = E\psi$  with  $E = E'$ ;

$$g_{\bar{k}} [\bar{\psi}_{\bar{0}}(\bar{r})]_m = [\bar{\psi}_{\bar{0}}(\bar{r} + A\bar{k})]_m; \tag{2.28}$$

and  $(J_{\bar{k}})_{mm}$  is a number. Equation (2.27) then, implies the existence of a solution  $\psi(\bar{r})$  to  $H\psi = E\psi$  with  $E = E'$ , which has the property that

$$g_{\bar{k}} \psi(\bar{r}) = \psi(\bar{r} + A\bar{k}) = (J_{\bar{k}})_{mm} \psi(\bar{r}). \tag{2.29}$$

$(J_{\bar{k}})_{mm}$  is the  $\bar{k}$ 'th element of one of the irreducible representations of the group  $G$  of translations ( $g_{\bar{n}}$ ). But the  $n$ 'th element of the irreducible representation characterized by the triple of numbers  $\bar{\beta}$  is given by

$$g_{\bar{n}} \rightleftharpoons e^{i\bar{\beta} \cdot \bar{j}_{\bar{n}}}, \tag{2.30}$$

where we now label the elements of  $G$  by a single subscript. We note here that

$$\begin{aligned}
g_{\bar{n}} g_{\bar{m}} &= g_{\bar{n}+\bar{m}} \rightleftharpoons (e^{i\bar{\beta} \cdot \bar{j}_{\bar{n}}}) (e^{i\bar{\beta} \cdot \bar{j}_{\bar{m}}}) = e^{i\bar{\beta} \cdot (\bar{j}_{\bar{n}} + \bar{j}_{\bar{m}})}, \\
\end{aligned} \tag{2.31}$$

and also that for inequivalent representations we need

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LECTURE 1: THE PHILOSOPHER'S TOOLBOX

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1.12. THE PHILOSOPHER'S TOOLBOX

1.13. THE PHILOSOPHER'S TOOLBOX

consider only those vectors  $\bar{\beta}$  in the range

$$-\pi \leq \beta_i \leq \pi. \quad (2.32)$$

Equation (2.29) now yields

$$g_n \psi(\bar{r}) = \psi(\bar{r} + A\bar{j}_n) = e^{i\bar{\beta} \cdot \bar{j}_n} \psi(\bar{r}). \quad (2.33)$$

Consider now the function

$$u_{\bar{\beta}}(\bar{r}) = e^{-i\bar{\beta} \cdot (A^{-1}\bar{r})} \psi(\bar{r}). \quad (2.34)$$

$$\begin{aligned} u_{\bar{\beta}}(\bar{r} + A\bar{j}) &= e^{-i\bar{\beta} \cdot (A^{-1}(\bar{r} + A\bar{j}))} \psi(\bar{r} + A\bar{j}) \\ &= e^{-i\bar{\beta} \cdot (A^{-1}\bar{r})} \psi(\bar{r}) \\ &= u_{\bar{\beta}}(\bar{r}). \end{aligned} \quad (2.35)$$

If we now let

$$(A^{-1})^T \bar{\beta} = \bar{k} \quad (2.36)$$

and define

$$u_{\bar{k}}(\bar{r}) = u_{\bar{\beta}}(\bar{r}), \quad (2.37)$$

equations (2.34) and (2.35) imply that we can write  $\psi(\bar{r})$  in the form

$$\psi(\bar{r}) = e^{i\bar{k} \cdot \bar{r}} u_{\bar{k}}(\bar{r}) \quad (2.38)$$

where  $u_{\bar{k}}(\bar{r} + A\bar{n}) = u_{\bar{k}}(\bar{r})$ ; that is  $u_{\bar{k}}$  is periodic with the same period as  $V(\bar{r})$ . This, of course, is the well known theorem due to Bloch (1928). (Jones (1960), Lomont (1959)).





The inequalities

$$-\pi \leq \beta_i \leq \pi \quad (2.32)$$

clearly provide one acceptable volume  $V$  over which the vector  $\beta$  may range to generate all inequivalent irreducible representations of the translation group  $G$ . It is also clear that  $V$  is not the only acceptable volume. In fact, any volume (or set of disconnected volumes) which is equivalent to  $V$  will suffice, where the points with coordinates  $\beta_i$  and those with coordinates  $\beta_i + 2\pi n_i$  are said to be equivalent.

### The Reciprocal Lattice; Brillouin Zones

Let us set

$$A^{-1} = B \quad (2.39)$$

and define the column vectors of  $2\pi B^T$  to be the basis vectors of a lattice in "k-space" or "reciprocal space". From equation (2.36) we see that if

$$\beta = 2\pi \bar{n}, \quad (2.40)$$

that is, a lattice point of a simple cubic lattice of side  $2\pi$ , then

$$(\bar{k})^T = (\bar{n})^T (2\pi B), \quad (2.41)$$

or

$$\bar{k} = (2\pi B)^T \bar{n}. \quad (2.42)$$

That is,  $\bar{k}$  is a lattice point of the reciprocal lattice. As  $\beta$  ranges through a unit cubic cell in  $\beta$ -space,  $\bar{k}$  ranges through a corresponding rhombohedral unit cell in k-space. If in



$\beta$ -space the unit cell has a lattice point at its geometrical center, so does the corresponding unit cell in  $k$ -space. If the  $\beta$ -space unit cell has lattice points at its corners, so must the  $k$ -space unit cell. However, the most symmetric unit cell in  $\beta$ -space, a cube, does not correspond (except accidentally) to the most symmetric unit cell in  $k$ -space.

The most symmetric unit cell in  $k$ -space is easily found. The vector  $(2\pi B)^T \bar{n}$ , in  $k$ -space, defines a lattice point, and the equation

$$\bar{k} \cdot [(2\pi B)^T \bar{n}] = (1/2) |(2\pi B)^T \bar{n}|^2 \quad (2.43)$$

defines a plane which bisects perpendicularly the line joining  $\bar{k} = \bar{0}$  to the lattice point specified by  $\bar{n}$ . Simplifying equation (2.43) yields

$$\bar{k} \cdot B^T \bar{n} = \pi \bar{n} \cdot B^T B \bar{n}; \quad (2.44)$$

the smallest volume enclosed by these planes, as  $\bar{n}$  varies over all non-zero integer vectors, is the most symmetric unit cell in  $k$ -space. This cell is also, by definition, the first Brillouin Zone of the space lattice characterized by  $A$ . (Brillouin (1953), Jones (1960)).

As  $\bar{k}$  ranges over the first Brillouin zone in reciprocal space,  $\bar{\beta}$ , in general, ranges over some unsymmetric unit cell in  $\beta$ -space. Figures 1, 2 and 3 illustrate the relation among real space, reciprocal space and  $\beta$ -space lattices for the case of a plane hexagon.

From equations (2.36) and (2.38) it is clear that  $E$  may be regarded as a function of  $\bar{k}$  or  $\bar{\beta}$ . The advantage of considering  $E(\bar{\beta})$  lies in the simple volume over which it is necessary to allow  $\bar{\beta}$  to range. It will be shown, however, that  $E(\bar{k})$  possesses certain symmetry properties, and these make it desirable to investigate the nature of  $E$  as a function of  $\bar{k}$  rather than  $\bar{\beta}$ .



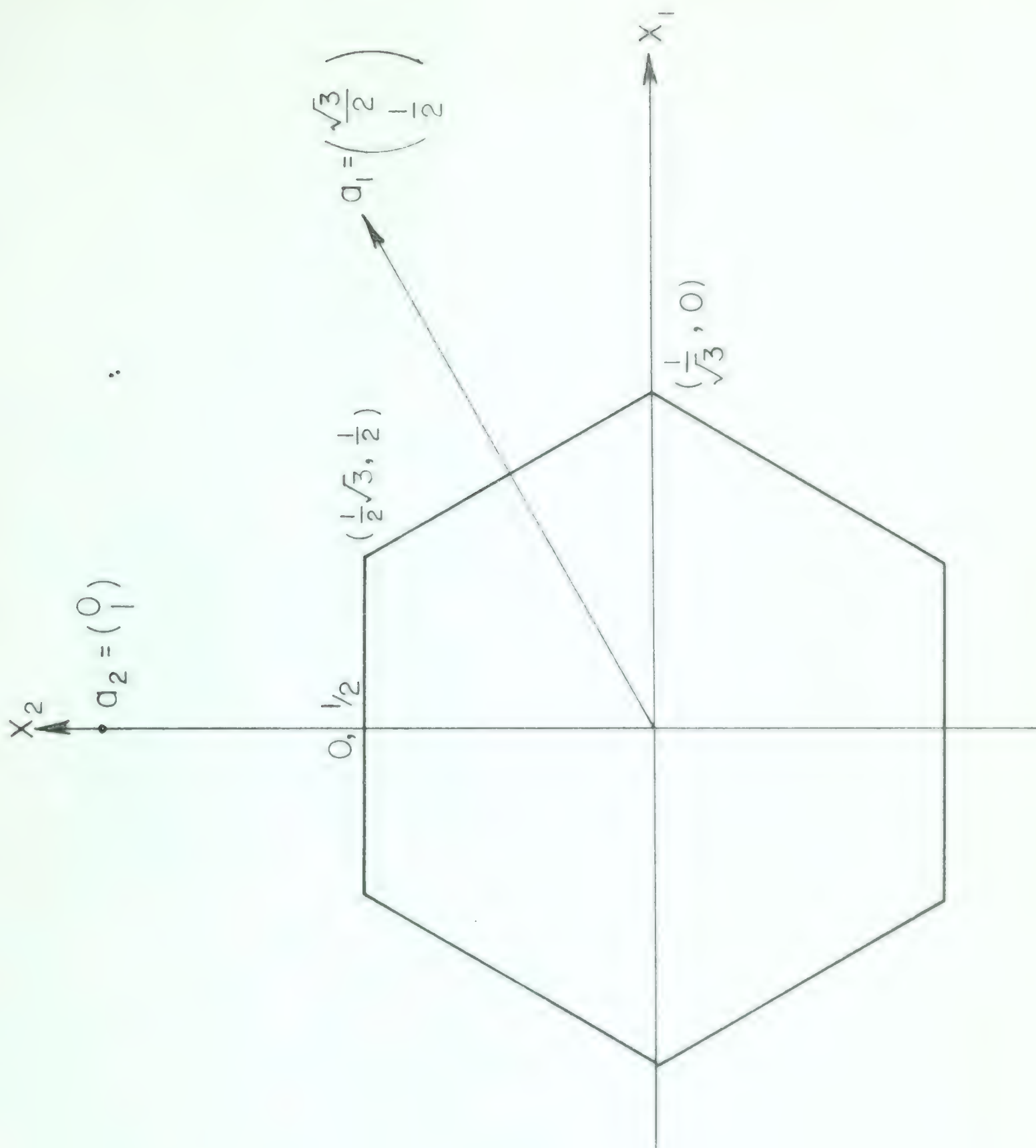


## FIGURE 1

## The Plane Hexagonal Lattice

The hexagon shown is the Wigner-Seitz cell for the hexagonal lattice with basis vectors  $\bar{a}_1$  and  $\bar{a}_2$ .







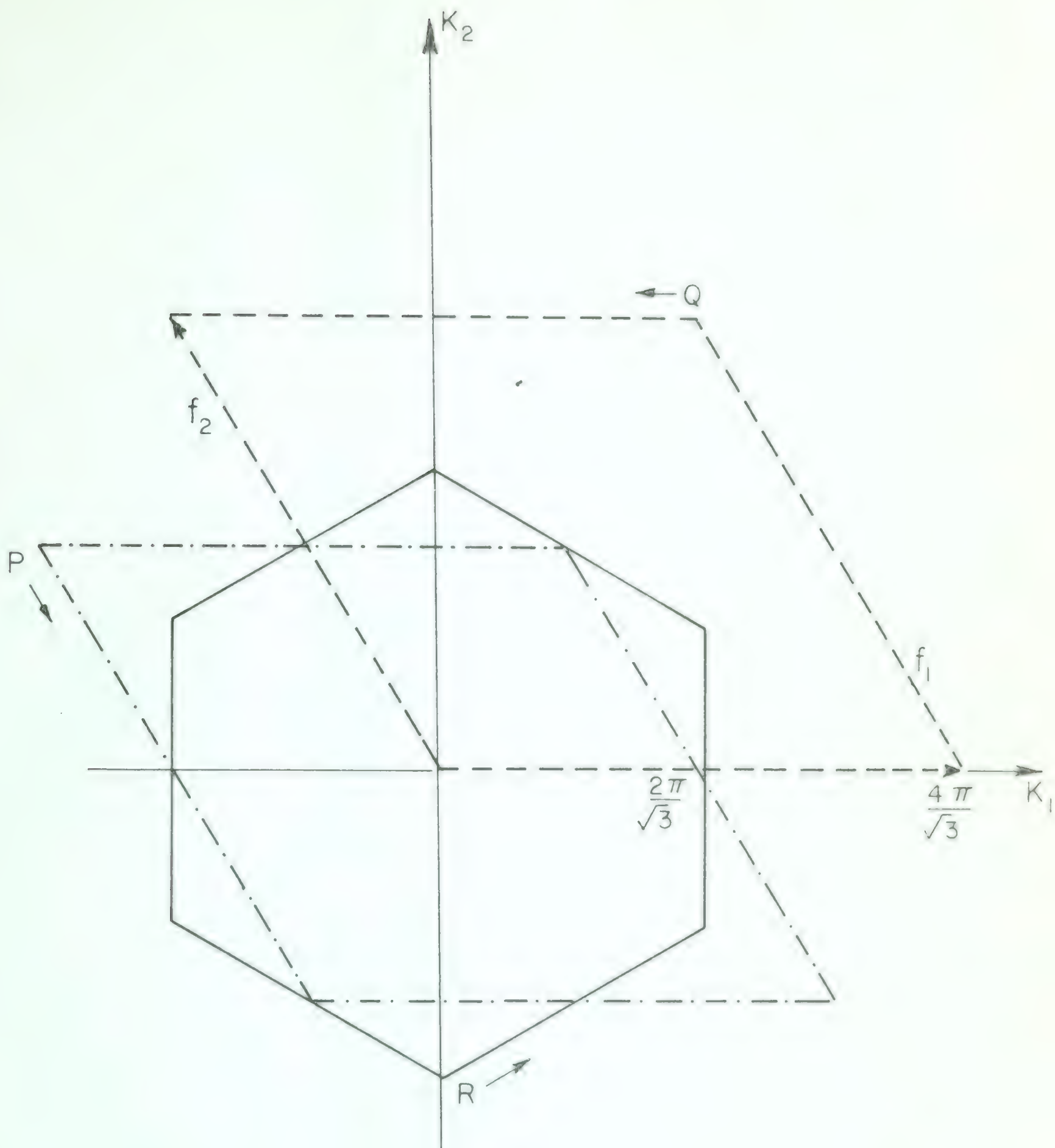


## FIGURE 2

## Reciprocal Space Lattice

The hexagon drawn in solid lines is the first Brillouin zone for the plane hexagonal lattice illustrated in Figure 1.  $\bar{f}_1$  and  $\bar{f}_2$  are the reciprocal lattice vectors. The point R and direction indicated correspond to the point R and direction on the polygon drawn in solid lines in Figure 3. The points P and Q (and directions) on the two rhombuses correspond to the points P and Q (and directions) on the two squares in Figure 3.







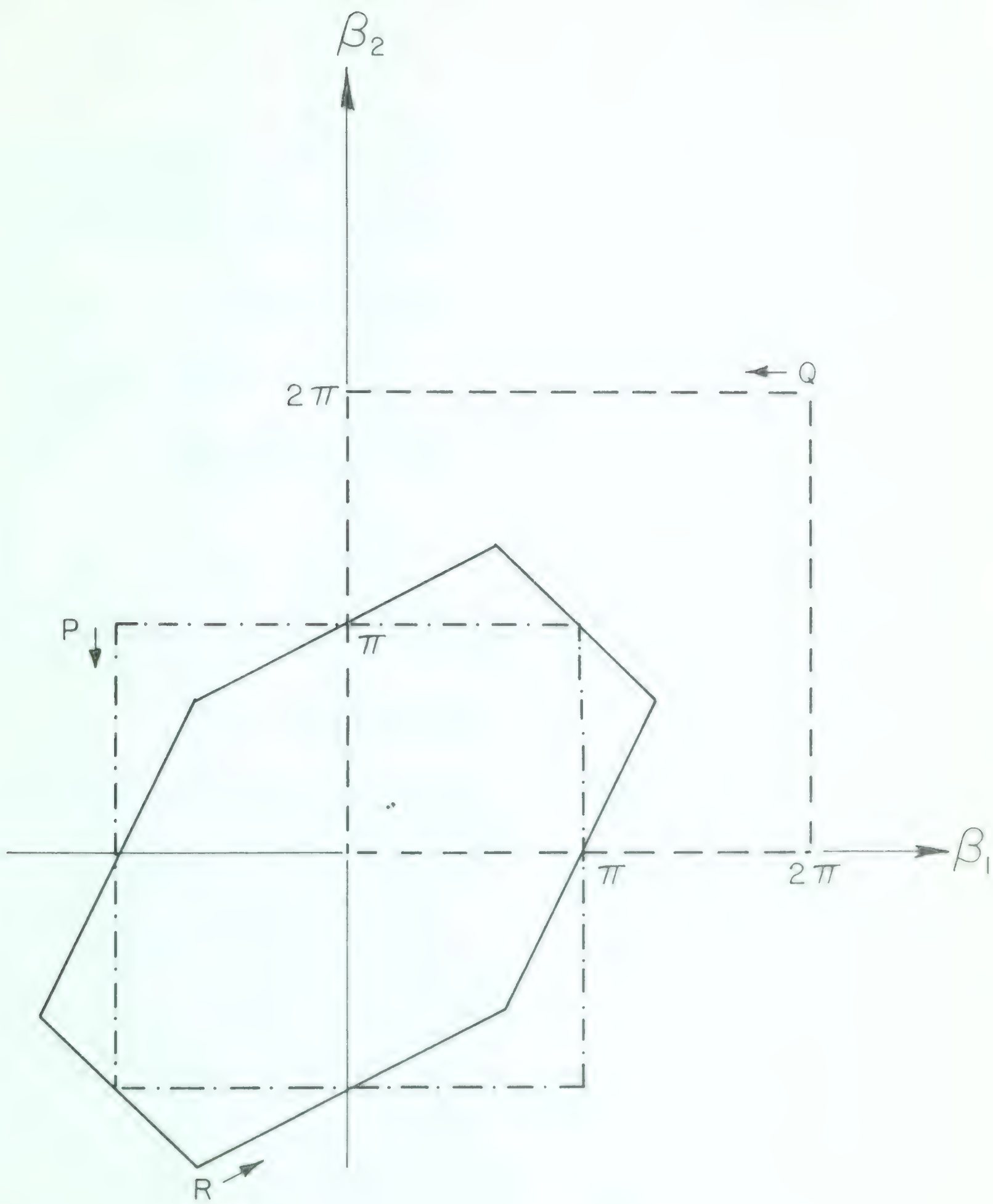


## FIGURE 3

The  $\beta$ -Space Lattice

The three cells shown correspond to the three k-space cells in Figure 2.







### Energy Band Structure

Assuming that  $\psi(\vec{r})$  is a bloch wave function, we have

$$\psi = e^{i\vec{k} \cdot \vec{r}} u(\vec{r}) \quad (2.45)$$

where we suppress the subscript  $\vec{k}$  in  $u_{\vec{k}}(\vec{r})$ . Since  $u$  must be a periodic function of  $\vec{r}$  with the same period as  $V$ , we may expand  $u$  in a Fourier series of the form

$$u(\vec{r}) = \sum_{\vec{n}} c_{\vec{n}} e^{-2\pi i \vec{n} \cdot B \vec{r}}. \quad (2.46)$$

And we see that

$$\begin{aligned} u(\vec{r} + A\vec{m}) &= \sum_{\vec{n}} c_{\vec{n}} e^{-2\pi i \vec{n} \cdot B(\vec{r} + A\vec{m})} \\ &= u(\vec{r}), \end{aligned} \quad (2.47)$$

since  $AB = I$ . Substituting (2.45) into  $H\psi = E\psi$ , we get

$$\nabla^2 u + 2i\vec{k} \cdot \nabla u + (E - \vec{k} \cdot \vec{k} - V)u = 0. \quad (2.48)$$

If we now substitute (2.46) into (2.48) we get

$$\sum_{\vec{n}} c_{\vec{n}} e^{-2\pi i \vec{n} \cdot B \vec{r}} (E - \vec{k}_{\vec{n}} \cdot \vec{k}_{\vec{n}} - V) = 0, \quad (2.49)$$

where we have defined

$$\vec{k}_{\vec{n}} = \vec{k} - 2\pi B^T \vec{n}. \quad (2.50)$$

If we assume an almost empty lattice, or

$$|E| \gg |V|, \quad (2.51)$$

we expect that





$$u(r) \sim C_{\bar{s}} e^{2\pi i \bar{s} \cdot B\bar{r}} \quad (2.52)$$

in which case

$$\psi(\bar{r}) \sim C_{\bar{s}} e^{i\bar{k} \cdot \bar{r}} e^{2\pi i \bar{s} \cdot B\bar{r}} = C_{\bar{s}} e^{i\bar{k}\bar{s} \cdot \bar{r}}, \quad (2.53)$$

and we expect, then, that

$$E \sim |\bar{k}_{\bar{s}}|^2. \quad (2.54)$$

The following material closely parallels that given by Mott and Jones (1958), the essential difference being that they consider only the case  $\bar{s} = \bar{0}$ . In (2.49), then, we neglect all terms  $VC_{\bar{n}}$ ,  $\bar{n} \neq \bar{s}$  as compared with  $VC_{\bar{s}}$ ; we get

$$VC_{\bar{s}} = \sum_{\bar{n} \neq \bar{s}} C_{\bar{n}} e^{-2\pi i \bar{n} \cdot B\bar{r}} (E - \bar{k}_{\bar{n}} \cdot \bar{k}_{\bar{n}}). \quad (2.55)$$

Multiplying both sides of (2.55) by  $e^{2\pi i \bar{m} \cdot B\bar{r}}$  and integrating over one unit cell of volume  $v$ , we find

$$C_{\bar{s}} \int V(\bar{r}) e^{2\pi i \bar{m} \cdot B\bar{r}} d\tau = C_{\bar{m}} (E - \bar{k}_{\bar{m}} \cdot \bar{k}_{\bar{m}}) v, \quad (2.56)$$

since the  $e^{2\pi i \bar{n} \cdot B\bar{r}}$ , being solutions of the Helmholtz equation with periodic boundary conditions, must form an orthogonal set for different values of  $\bar{m} \cdot B^T B \bar{m}$ . The only terms which might survive, then are those for which  $\bar{n} = \pm \bar{m}$ . The product, when  $\bar{n} = -\bar{m}$  is  $e^{2\pi i (2\bar{m}) \cdot B\bar{r}}$ , which must be orthogonal to unity, and (2.56) follows.

Let us now define

$$V_{\bar{m}} = (1/v) \int V(\bar{r}) e^{2\pi i \bar{m} \cdot B\bar{r}} d\tau. \quad (2.57)$$

Equation (2.56) becomes

$$C_{\bar{s}} V_{\bar{m}} = C_{\bar{m}} (E - |\bar{k}_{\bar{m}}|^2). \quad (2.58)$$

The first part of the paper discusses the importance of the study and the objectives of the research. It also provides a brief overview of the methodology used in the study. The second part of the paper presents the results of the study and discusses the implications of the findings. The third part of the paper concludes the study and provides some suggestions for future research.

The study was conducted in a laboratory setting and involved a series of experiments. The results of the experiments are presented in the following table:

Experiment	Results
Experiment 1	Results of Experiment 1
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If we now put  $\bar{m} = \bar{s}$  we find

$$E = |\bar{k}_{\bar{s}}|^2 + V_{\bar{s}} \quad (2.59)$$

which agrees with our expected value  $E \sim |\bar{k}_{\bar{s}}|^2$ .  
Solving for  $C_{\bar{m}}$  we find

$$C_{\bar{m}} = \frac{C_{\bar{s}} V_{\bar{m}}}{E - |\bar{k}_{\bar{m}}|^2} = \frac{C_{\bar{s}} V_{\bar{m}}}{|\bar{k}_{\bar{s}}|^2 - |\bar{k}_{\bar{m}}|^2 + V_{\bar{s}}}, \quad \bar{m} \neq \bar{s}. \quad (2.60)$$

This approximation for  $C_{\bar{m}}$  can only be valid if  $|C_{\bar{m}}| \ll |C_{\bar{s}}|$ , and this is clearly not the case when

$$|\bar{k}_{\bar{s}}|^2 - |\bar{k}_{\bar{m}}|^2 = 0. \quad (2.61)$$

Substituting equation (2.50) into (2.61) yields

$$\bar{k} \cdot B^T(\bar{m} - \bar{s}) = \pi(\bar{m} - \bar{s}) \cdot B^T B(\bar{m} - \bar{s}). \quad (2.62)$$

If  $\bar{s} = \bar{0}$ , equation (2.62) is identical to equation (2.44), which defines the boundaries of the Brillouin zones. Taking  $\bar{s} \neq \bar{0}$  merely corresponds to translating the reciprocal lattice by an integer linear combination of its lattice vectors.

We have found, then, that if  $|E| \gg |V|$ , the solution to (2.1) is closely approximated by

$$\psi(\bar{r}) = C_{\bar{s}} e^{i\bar{k}_{\bar{s}} \cdot \bar{r}} \quad (2.53)$$

and

$$E_{\bar{s}} = |\bar{k}_{\bar{s}}|^2 + V_{\bar{s}} \quad (2.59)$$





except near the boundary of a Brillouin zone.

If  $\bar{k}$  is near the boundary of a zone, the above calculations are, of course, invalid. In this region we approximate to  $\psi$  by the function

$$\begin{aligned}\psi(\bar{r}) &= e^{i\bar{k}\cdot\bar{r}}(C_{\bar{s}}e^{-2\pi i\bar{s}\cdot B\bar{r}} + C_{\bar{m}}e^{-2\pi i\bar{m}\cdot B\bar{r}}) \\ &= C_{\bar{s}}e^{i\bar{k}_{\bar{s}}\cdot\bar{r}} + C_{\bar{m}}e^{i\bar{k}_{\bar{m}}\cdot\bar{r}},\end{aligned}\quad (2.63)$$

that is, we retain only the two large coefficients of  $u$ . Substituting (2.63) into  $H\psi = E\psi$  we find

$$C_{\bar{s}}e^{i\bar{k}_{\bar{s}}\cdot\bar{r}}(E - |\bar{k}_{\bar{s}}|^2 - V) + C_{\bar{m}}e^{i\bar{k}_{\bar{m}}\cdot\bar{r}}(E - |\bar{k}_{\bar{m}}|^2 - V) = 0. \quad (2.64)$$

If we now multiply this equation by  $e^{-i\bar{k}_{\bar{s}}\cdot\bar{r}}$  and integrate over a unit cell we find

$$C_{\bar{s}}(E - |\bar{k}_{\bar{s}}|^2 - V_{\bar{o}}) - C_{\bar{m}}V_{\bar{s}-\bar{m}} = 0. \quad (2.65)$$

Similarly, for  $e^{-i\bar{k}_{\bar{m}}\cdot\bar{r}}$  we get

$$-C_{\bar{s}}V_{\bar{m}-\bar{s}} + C_{\bar{m}}(E - |\bar{k}_{\bar{m}}|^2 - V_{\bar{o}}) = 0. \quad (2.66)$$

To obtain non-trivial solutions  $C_{\bar{s}}$  and  $C_{\bar{m}}$  from (2.65) and (2.66), we find

$$(E - |\bar{k}_{\bar{m}}|^2 - V_{\bar{o}})(E - |\bar{k}_{\bar{s}}|^2 - V_{\bar{o}}) - |V_{\bar{m}-\bar{s}}|^2 = 0. \quad (2.67)$$

Near  $\bar{k}_{\bar{s}} = \bar{k}_{\bar{m}}$ , that is when  $\bar{k}$  is near the boundary of a Brillouin zone, we find from (2.67)



$$E = \frac{|\bar{k}_{\bar{m}}|^2 + |\bar{k}_{\bar{s}}|^2}{2} + V_0 \pm (1/2) \left[ (|\bar{k}_{\bar{m}}|^2 - |\bar{k}_{\bar{s}}|^2)^2 + 4 V_{\bar{m}-\bar{s}}^2 \right]^{1/2} \quad (2.68)$$

Then, on the boundary of the Brillouin zone defined by  $\bar{k}_{\bar{s}} = \bar{k}_{\bar{m}}$ , there is a gap in the permissible energies of width

$$\Delta E = 2 |V_{\bar{m}-\bar{s}}|, \quad (2.69)$$

the nearest permissible energies being given by

$$E = |\bar{k}_{\bar{s}}|^2 + V_0 \pm |V_{\bar{m}-\bar{s}}|. \quad (2.70)$$

There is, however, no energy discontinuity across the zone boundary, since (2.68) is symmetric in  $\bar{m}$  and  $\bar{s}$ . The energy discontinuity pointed out by Mott and Jones (1958) results from their considering  $\bar{s} = \bar{0}$  only.

Figure 4 illustrates the situation in one demension, where  $V(x) = V(x+na)$ , and  $V(-x) = V(x)$ . We see that the  $(E,k)$  relationship for the empty lattice is given by the parabolas

$$E = \left(k - \frac{2n\pi}{a}\right)^2, \quad n = 0, \pm 1, \pm 2, \dots \quad (2.71)$$

A small periodic potential perturbs the  $(E,k)$  relationship in such a fashion that the continuous range of permissible energies

$$V_0 = 0 \leq E \leq \frac{\pi^2}{a^2}, \quad \frac{\pi^2}{a^2} \leq E \leq \frac{4\pi^2}{a^2}, \quad \frac{4\pi^2}{a^2} \leq E \leq \frac{9\pi^2}{a^2}, \dots \quad (2.72)$$

shrinks to the band structure



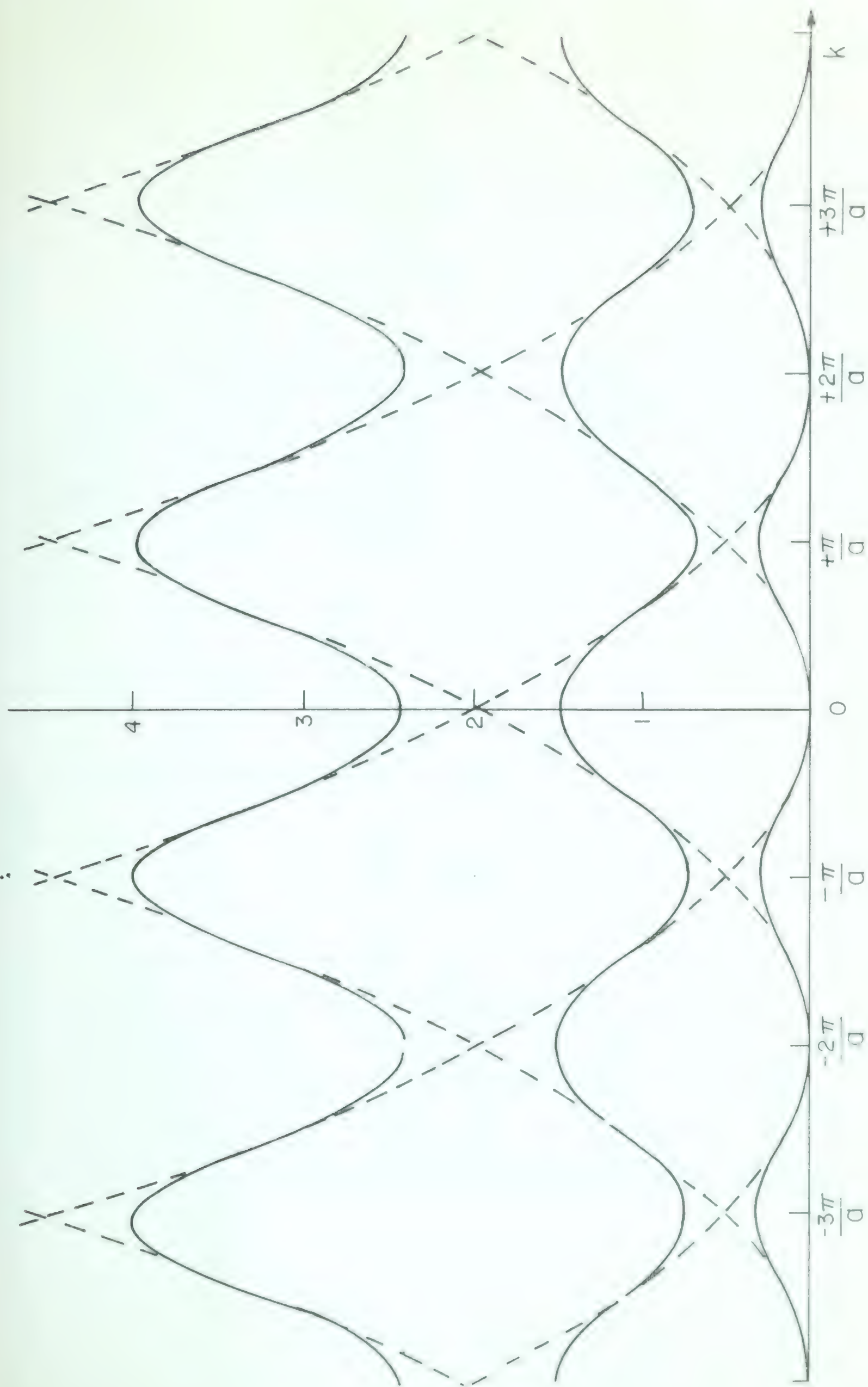
FIGURE 4

## Dispersion Relations in One Dimension

The dashed curves are the parabolas  $E = (k - 2n\pi/a)^2$  and are the  $(E, \bar{k})$  relation for an empty lattice. The solid curves represent the perturbed  $(E, \bar{k})$  relation for a small periodic potential.









$$V_0 \leq E \leq \frac{\pi^2}{a^2} - |V_1|, \quad \frac{\pi^2}{a^2} + |V_1| \leq E \leq \frac{4\pi^2}{a^2} - |V_2|,$$

$$\frac{4\pi^2}{a^2} + |V_2| \leq E \leq \frac{9\pi^2}{a^2} - |V_3|, \dots \quad (2.73)$$

We note here, that in choosing  $\psi$  to be a Bloch wave function  $e^{i\bar{k} \cdot \bar{r}} u_{\bar{k}}(\mathbf{r})$ , that it is not valid, even for very small periodic potentials, to regard  $\bar{k}$  as a momentum vector except along those sheets of the  $(E, k)$  relation near  $E = |\bar{k}|^2$ . Only when  $\bar{s}$  in equations (2.52), (2.53) and (2.54) is chosen to be  $\bar{0}$  is this true. In general,

$$\bar{p}\psi = -i\nabla\psi = \bar{k}\psi - ie^{i\bar{k} \cdot \bar{r}} \nabla u, \quad (2.74)$$

and  $\nabla u \neq 0$  unless  $\bar{s} = \bar{0}$ .

The free space Hamiltonian is, of course,  $-\nabla^2$ ; the empty lattice Hamiltonian is given by

$$H = \lim_{\epsilon \rightarrow 0} (-\nabla^2 + \epsilon V). \quad (2.75)$$

The eigensolutions to the two problems are quite different; the  $(E, k)$  relationship for the empty lattice is  $E = |\bar{k}_{\bar{s}}|^2$  for any integer vector  $\bar{s}$ , whereas the free space solution admits only  $\bar{s} = \bar{0}$ . Free space is, of course, unable to exchange momentum with an electron, and the momentum is indeed  $\bar{k}$ . But a lattice, on the other hand no matter how small the potential,





possesses infinite inertia and is able, by means of Umklapp processes, to exchange momentum with an electron. The momentum of the entire system is, of course, conserved. (Peierls (1956)).

### Wave Function Symmetry

Since  $V(\bar{r} + A\bar{n}) = V(\bar{r})$  for any integer vector  $\bar{n}$ , there exists a group of rotations, proper and improper, which leaves  $V$  and therefore  $H$ , invariant.

We will superimpose a co-ordinate system on the lattice, and rotate the co-ordinate system leaving the lattice unchanged. Let  $\bar{r}$  be any vector in the original coordinate system, and let

$$\bar{r}' = S\bar{r} \quad (2.76)$$

be the same vector in the rotated coordinate system. The matrix  $S$ , then, characterizes the rotation under consideration. Only certain matrices  $S$  leave  $V$  unchanged, and these might be determined in the following fashion.

In the unrotated system the lattice basis vectors are  $\bar{a}_i$ , which are the column vectors of the matrix  $A$ . Any point  $N$  given by the vector

$$\bar{N} = \sum_i n_i \bar{a}_i = A\bar{n} \quad (2.77)$$

is a lattice point, where, of course, the components of the integer vector  $\bar{n}$  are  $(n_i)$ . If we now rotate the coordinate system by the matrix  $S$ , the point  $N$  in the rotated system is given by

$$\bar{N}' = S\bar{N} = SA\bar{n}. \quad (2.78)$$



The basis vectors, called  $\bar{a}_i'$  in the new coordinate system are given by

$$\bar{a}_i' = S\bar{a}_i \quad (2.79)$$

and therefore

$$A' = SA \quad (2.80)$$

and

$$A = S^{-1}A' = S^T A' \quad (2.81)$$

since  $S$  must be orthogonal. We find, then, that the point  $N$  is given by

$$\bar{N}' = A' \bar{n} \quad (2.82)$$

in the new coordinate system. If we now consider the vector  $\bar{N}$ , and rotate it along with the co-ordinate system to get a new vector  $\bar{M}$ , it defines a new point  $M$  the coordinates of which one found from

$$\bar{M} = A\bar{n} = S^T A' \bar{n} \equiv A' \bar{m} \quad (2.83)$$

in the rotated system. If we now insist that  $M$  also be a lattice point, for every integer choice of the vector  $\bar{n}$ , then we are insisting that equation (2.83), rewritten as

$$A' \bar{n} = S A' \bar{m} \quad (2.84)$$



have integer solutions  $\bar{m}$  for every integer  $\bar{n}$ . Equation (2.84) reduces to

$$A\bar{n} = SA\bar{m} \quad (2.85)$$

Any  $S$  which allows of such solutions characterizes a permissible rotation.

In practice of course, most if not all of the rotations which leave  $H$  invariant are readily determined by an inspection of the lattice.

Let us consider, now, the point group of the lattice  $G$ , with elements  $g_n$ ,  $n = 1, 2, \dots, N$ , where each  $g_n$  is a rotation and/or reflection which leaves  $H = -\nabla^2 + V$  invariant. That is

$$g_n H f = H g_n f, \quad n = 1, 2, \dots, N. \quad (2.86)$$

By definition

$$g_n f(\bar{r}) = f(S_n \bar{r}) \quad (2.87)$$

Where  $S_n$  is the matrix which characterizes the appropriate rotation and/ or reflection. As in the development of Bloch's theorem, we assume that  $\varphi(\bar{r})$  is a solution, for  $E = E'$ , to  $H\psi = E\psi$ ; i.e.

$$H\varphi = E'\varphi. \quad (2.88)$$

Operating by  $g_j$  we find

$$g_j H \varphi(\bar{r}) = H g_j \varphi(\bar{r}) = H \varphi(S_j \bar{r}) \quad (2.89)$$





and

$$g_j E' \varphi(\bar{r}) = E' g_j \varphi(\bar{r}) = E' \varphi(S_j \bar{r}) ; \quad (2.90)$$

therefore

$$H\varphi(S_j \bar{r}) = E' \varphi(S_j \bar{r}). \quad (2.91)$$

That is

$$\varphi_j(\bar{r}) \equiv g_j \varphi(\bar{r})$$

is also a solution with  $E = E'$  to (2.1). Then, given a solution  $\varphi$  we can generate a total of  $N$  solutions, not necessarily distinct,  $\varphi_j$ ,  $j = 1, 2, \dots, N$  of  $H\psi = E\psi$  all corresponding to  $E = E'$ .

Define, now, the row vector  $\bar{\varphi}^T(\bar{r})$  to be

$$\bar{\varphi}^T(\bar{r}) = [\varphi_1(\bar{r}), \varphi_2(\bar{r}), \dots, \varphi_N(\bar{r})], \quad (2.92)$$

and define the operation of  $g_k$  on  $\bar{\varphi}^T$  as

$$g_k \bar{\varphi}^T = [g_k \varphi_1, g_k \varphi_2, \dots, g_k \varphi_N] \quad (2.93)$$

We note that

$$g_k \varphi_j = g_k g_j \varphi = g_m \varphi = \varphi_m \quad (2.94)$$

for some  $m$ ,  $1 \leq m \leq N$ . We now define

$$\bar{\varphi}_k(\bar{r}) \equiv g_k \varphi(\bar{r}) \quad (2.95)$$



so that  $\bar{\varphi}_k$  is a vector the components of which are a permutation of those of  $\bar{\varphi}$ . We now let  $G_j$ ,  $j = 1, 2, \dots, N$  be a set of  $N \times N$  permutation matrices forming the regular representation of  $G$ , and we choose the subscripts so that

$$G_k \bar{\varphi}(\bar{r}) = \bar{\varphi}_k(\bar{r}) = g_k \varphi(\bar{r}) \quad (2.96)$$

Again we perform a similarity transformation on the regular representation  $(G_j)$  to get a completely reduced representation  $(J_j)$ , where

$$J_j \equiv S G_j S^{-1}. \quad (2.97)$$

Again we note that  $G_k^\varphi = \bar{\varphi}_k \rightarrow (S G_k S^{-1})(S \bar{\varphi}) = (S \bar{\varphi}_k)$ , that is

$$J_k \bar{\psi} = \bar{\psi}_k \quad (2.98)$$

where

$$\bar{\psi} = S \bar{\varphi} \quad (2.99)$$

and

$$\bar{\psi}_k \equiv S \bar{\varphi}_k. \quad (2.100)$$

It is clear that the components of  $\bar{\psi}_k(\bar{r})$  are individually solutions to (2.1) with  $E = E'$ .

Now, since the  $J$ 's are completely reduced, that is, each  $J_m$  is of the form





$$\begin{pmatrix} J_m^{(1)} & & & \\ & J_m^{(2)} & & 0 \\ & & \ddots & \\ 0 & & & J_m^{(s)} \end{pmatrix}$$

where the size of the block  $J_m^{(k)}$  depends on  $k$  but not on  $m$ , and no further reduction is possible, the set  $(J_m^{(k)})_{m=1,2,\dots,N}$  forms an irreducible representation of  $G$ . This is true for each  $k$ , but the representations for different  $k$  may be equivalent. It can be shown in general that the regular representation reduces to give each  $t \times t$  representation  $t$  times (Hamermesh (1962)). Since  $G$  represents the point group of a lattice, no irreducible representations are of order more than three.

Let us assume, now, that  $g_1$  is the identity operator. One of the irreducible representations, say the first, must be the identity representation; that is

$$J_m^{(1)} = 1, \quad m = 1, 2, \dots, N. \quad (2.101)$$

And since

$$J_m^{(1)} \bar{\psi}_1(\bar{r}) = g_m \bar{\psi}_1(\bar{r}) = \bar{\psi}_1(S_m \bar{r}), \quad (2.102)$$

then

$$J_m^{(1)} [\bar{\psi}_1(\bar{r})]_1 = [\bar{\psi}_1(S_m \bar{r})]_1. \quad (2.103)$$



But  $J_m^{(1)} = 1$  for all  $m$ ; equation (2.103), then implies that the first component of  $\bar{\psi}_1(\bar{r})$ , call it  $\theta(\bar{r})$ , is a solution to (2.1) with  $E = E'$  such that

$$\theta(S_m \bar{r}) = \theta(\bar{r}). \quad (2.104)$$

$S_m$ , here is any rotation or reflection which leaves  $H$  invariant.

Another irreducible representation, say the second, might be an alternating representation, that is

$$\begin{aligned} J_m^{(2)} &= 1 \quad \text{for some } m, 1 \leq m \leq M \\ J_m^{(2)} &= -1 \quad \text{for the remaining } m. \end{aligned} \quad (2.105)$$

Then the second component of  $\bar{\psi}_1(\bar{r})$ , call it  $\Theta(\bar{r})$  is a solution such that

$$\begin{aligned} \Theta(S_m \bar{r}) &= \Theta(\bar{r}) \quad \text{if } J_m^{(2)} = 1, \\ &= -\Theta(\bar{r}) \quad \text{if } J_m^{(2)} = -1. \end{aligned} \quad (2.106)$$

If the third irreducible representation is also 1 by 1, the  $J_m^{(3)}$  must be of the form

$$J_m^{(3)} = e^{i\alpha_m} \quad (2.107)$$

for some set of real numbers  $(\alpha_m)$ . In this case  $[\psi_1(\bar{r})]_3$  is a solution which has the property that

$$[\psi_1(S_m \bar{r})]_3 = e^{i\alpha_m} [\psi_1(\bar{r})]_3 \quad (2.108)$$



Let us assume, now, that the  $(J_m^{(4)})$  form a 2x2 irreducible representation. Rename the fourth and fifth components of  $\bar{\psi}_1(\bar{r})$   $\xi(\bar{r})$  and  $\zeta(\bar{r})$  respectively. Then

$$J_m^{(4)} \begin{pmatrix} \xi \\ \zeta \end{pmatrix} = \begin{pmatrix} (J_m^{(4)})_{11}\xi + (J_m^{(4)})_{12}\zeta \\ (J_m^{(4)})_{21}\xi + (J_m^{(4)})_{22}\zeta \end{pmatrix}; \quad (2.109)$$

but this must be the same as

$$g_m \begin{pmatrix} \xi(\bar{r}) \\ \zeta(\bar{r}) \end{pmatrix} = \begin{pmatrix} \xi(S_m(\bar{r})) \\ \zeta(S_m(\bar{r})) \end{pmatrix}. \quad (2.110)$$

That is  $\xi$  and  $\zeta$  must be pair of solutions such that

$$\begin{aligned} \xi(S_m \bar{r}) &= (J_m^{(4)})_{11} \xi(\bar{r}) + (J_m^{(4)})_{12} \zeta(\bar{r}) \\ \zeta(S_m \bar{r}) &= (J_m^{(4)})_{21} \xi(\bar{r}) + (J_m^{(4)})_{22} \zeta(\bar{r}). \end{aligned} \quad (2.111)$$

Thus, the irreducible representations of the point group of the lattice determine the possible symmetries of the solutions to  $H\psi = E\psi$ .

The above considerations refer to solutions of  $H\psi = E\psi$  which are not necessarily in the Bloch form. If we do insist that our solutions be of the form  $e^{i\bar{k}\cdot\bar{r}}u(\bar{r})$ , then we are interested only in those rotations which transform solutions into themselves, or linear combinations of other solutions belonging to the same  $\bar{k}$ . That is, we must restrict the group of operations to those which leave  $\bar{k}$  invariant, or change it into an equivalent  $\bar{k}$ .





If we rotate co-ordinates by a rotation characterized by  $S$ , the new coordinates of any point defined by  $\bar{r}$  are given by

$$\bar{r}' = S\bar{r} \quad (2.76)$$

And since

$$A \rightarrow A' = SA, \quad (2.80)$$

then

$$B \rightarrow B' = BS^T. \quad (2.112)$$

Since it is

$$(B')^T = SB^T \quad (2.113)$$

which characterizes the reciprocal lattice in the new coordinate system, it is clear that

$$\bar{k}' = S\bar{k}. \quad (2.114)$$

We insist, then, that given  $\bar{k}$ , the rotations  $S_m$  be confined to a subgroup  $G(\bar{k})$  of  $G$ , such that

$$S_m \bar{k} = \bar{k} + 2\pi B^T \bar{n}. \quad (2.115)$$

Clearly, for most vectors  $\bar{k}$  in the first Brillouin zone, the subgroup  $G(\bar{k})$  reduces to the identity element. However, for vectors  $\bar{k}$  along lines or planes of symmetry inside the zone,



there are other elements of  $G$  which leave  $\bar{k}$  invariant. And if  $\bar{k}$  is also on the zone boundary, there will be other elements of  $G$  which transform  $\bar{k}$  into an equivalent vector in reciprocal space.

Again, it is not too difficult to determine the subgroup  $G(\bar{k})$  given  $\bar{k}$ , by an inspection of the reciprocal lattice.

### The Symmetry of $E(\bar{k})$ ; Surfaces of Constant Energy

If  $\psi$  is of the Bloch form, then  $H\psi = E\psi$  yields

$$\nabla^2 u + 2i\bar{k} \cdot \nabla u + (E(\bar{k}) - \bar{k} \cdot k - V)u = 0. \quad (2.48)$$

If we now perform on the space coordinates a rotation characterized by the matrix  $S$ , we are in effect making the change of variable

$$\bar{r} = S^T \bar{r}'. \quad (2.76)$$

As we have seen, the space rotation induces a rotation in reciprocal space also characterized by  $S$ , so that

$$\bar{k} = S^T k'^{-1}. \quad (2.114)$$

Since equation (2.76) implies that

$$\nabla = S^T \nabla', \quad (2.116)$$

the various terms in (2.48) undergo the following transformations;

$$\nabla^2 = \nabla^T \nabla = (\nabla')^T S S^T \nabla' = (\nabla')^T \nabla' = (\nabla')^2; \quad (2.117)$$



$$\bar{k} \cdot \bar{k} = (\bar{k})^T (\bar{k}) = (\bar{k}')^T S S^T \bar{k}' = (\bar{k}')^T \bar{k}' = \bar{k}' \cdot \bar{k}'; \quad (2.118)$$

the well known results that neither  $\nabla^2$  nor the length of a vector are affected by rotations, proper or improper. Nor is the term  $\bar{k} \cdot \nabla$ :

$$\bar{k} \cdot \nabla = (\bar{k})^T \nabla = (\bar{k}')^T S S^T \nabla' = (\bar{k}')^T \nabla' = \bar{k}' \cdot \nabla' \quad (2.119)$$

If we now insist that  $S$  be one of the rotations which leaves  $H$  invariant, equation (2.48), after dropping the primes, becomes

$$\nabla^2 u(S^T \bar{r}) + 2i \bar{k} \cdot \nabla u(S^T \bar{r}) + (E(S^T \bar{k}) - \bar{k} \cdot \bar{k} - V(\bar{r})) u(S^T \bar{r}) = 0. \quad (2.120)$$

This equation is of exactly the same form as equation (2.48), and since periodic boundary conditions are unaffected by rotations, we see that symmetrized solutions  $u(\bar{r})$  to equation (2.48) transform according to the irreducible representations of the entire point group of the lattice, and that  $E(\bar{k})$  is invariant under all operations of this group.

The symmetry of  $E$  with respect to  $\bar{k}$ , and the fact that  $E$  is an analytic function of  $\bar{k}$  except where different energy bands touch in  $k$ -space (Jones, 1960), greatly simplify the determination of the  $(E, \bar{k})$  relationship within the first Brillouin zone. In the case of the plane hexagon, for example one need consider only those  $\bar{k}$ 's within the triangle bounded





by

$$k_x = 0,$$

$$k_y = 1/2,$$

$$\text{and} \quad k_y = \sqrt{3}k_x. \quad (2.121)$$

The energy over the remainder of the zone is easily generated by suitable rotations and reflections, given the energy for  $\bar{k}$  inside this triangle. In general, a knowledge of  $E(\bar{k})$  where  $\bar{k}$  varies over some small fraction of the Brillouin zone provides one with  $E(\bar{k})$  over the entire zone.

Further, since  $E(\bar{k})$  is analytic and invariant under the operations of the point group of the lattice, surfaces of constant energy must intersect at right angles the various planes of symmetry of the Brillouin zone. And on the boundaries of the zone, non-degenerate energy bands must intersect the bounding plane at right angles.

The solid curves of Figure 4 provide an illustration in one dimension. The only "plane" of symmetry within the first Brillouin zone is the point  $k = 0$ , and the boundaries of the zone are at  $k = \pm\pi/a$ .



## CHAPTER III

### EXPERIMENTAL METHODS FOR DETERMINING FERMI SURFACES

In this chapter we consider three phenomena which are more or less amenable to experiment, and which enable one to gain a knowledge of some of the geometrical characteristics of the Fermi surface of the metal. To varying degrees of approximation, we concern ourselves below with the theoretical bases for the anomalous skin effect, cyclotron resonance, and the de Haas-van Alphen effect in that order.

#### The Anomalous Skin Effect

Consider the conduction of electricity near the surface of a semi-infinite slab of an isotropic metal. The surface of the metal is the x-y plane, and the current is being induced by an electric field of frequency  $\omega$ , plane polarized in the x direction, normal to the surface of the metal. Assuming that electrons which collide with the surface of the metal are reflected with  $k_x$  and  $k_y$  unchanged, and  $k_z$  replaced by  $-k_z$ , Pippard (1960) has shown that the surface impedance  $Z$  in the x direction is given by

$$Z = 8i\omega \int_0^{\infty} \frac{dv}{v^2 + 4\pi i\omega\sigma(v)} \quad (3.1)$$

Here, the conductivity is defined by

$$J_v = \sigma(v)E_v \quad (3.2)$$



and  $\xi_v$  and  $J_v$  are the Fourier components of  $\xi(z)$  and the current density  $J(z)$  (both in the  $x$  direction); that is

$$\xi(z) = \int_{-\infty}^{\infty} \xi_v e^{ivz} dv \quad (3.3)$$

and

$$J(z) = \int_{-\infty}^{\infty} J_v e^{ivz} dv. \quad (3.4)$$

If the free path  $l$  of an electron is short enough, then the only values of  $v$  which make a significant contribution to  $Z$  in (3.1) are those for which

$$vl \ll 1. \quad (3.5)$$

In this case  $\sigma(v)$  may be taken to be constant over the range with a value equal to the D. C. conductivity  $\sigma$ , and equation (3.1) is easily integrated to yield the normal skin effect

$$Z_n = (1+i)\sqrt{(2\pi\omega/\sigma)} \quad (3.6)$$

If, however, the free path of an electron is long enough, the significant values of  $v$  in (3.1) satisfy

$$vl \gg 1. \quad (3.7)$$

Pippard (1960) has shown that as  $v \rightarrow \infty$ ,  $\sigma(v)$  is given by

$$\sigma(v) = \frac{e^2}{4\pi^2 \hbar v} \int R(k_y) dk_y \quad (3.8)$$





where  $R(k_y)$  and the range of integration are determined as follows. Consider the curve formed by the intersection of the Fermi surface  $E(\bar{k}) = E_F$ , and a plane normal to  $k_y$ .  $R(k_y)$  is the sum of the absolute values of the radii of curvature of all points on this curve the tangents of which are parallel to the  $k_z$  axis. The minimum and maximum values of  $k_y$  are, of course, given by the extrmities of the Fermi surface in the  $k_y$  direction. In this case where  $v \rightarrow \infty$  (the extreme anomalous limit),  $Z$  is given by

$$Z_\infty = 8i\omega \int_0^\infty \frac{v dv}{v^3 + is^3}, \quad (3.9)$$

where

$$s = \frac{\omega e^{\epsilon}}{\pi \hbar} \int R(k_y) dk_y. \quad (3.10)$$

Equation (3.9) is easily integrated to give

$$Z_\infty = \frac{8\pi\omega}{3^{3/2}s} (1+i\sqrt{3}). \quad (3.11)$$

It was shown by Reuter and Sondheimer (1948) that assuming completely diffuse scattering at the metal surface, as opposed to specular reflection as above, leads to

$$Z = 4\pi^2 i\omega / \left[ \int_0^\infty \ln(1+4\pi i\omega v) dv \right], \quad (3.12)$$

which, in the extreme anomalous limit yields

$$Z_\infty = \frac{\sqrt{3}\pi\omega}{s} (1+i\sqrt{3}). \quad (3.13)$$



The impedences given by equations (3.11) and (3.13) differ by a factor of  $9/8$ ; the second seems more plausible from a consideration of the metal surface. In either case,  $Z$  depends only on the frequency of the applied electric field, and geometry of the Fermi surface. Measurement of  $Z$  for a variety of crystals orientations provides one with  $g$ , and hence  $\int R(k_y) dk_y$ .

As implied by Chambers (1956), reconstruction of the Fermi surface from a knowledge of this integral would indeed be a formidable task, and is not even possible unless the Fermi surface is both convex and centro-symmetric. The anomalous skin effect, then, would appear to be a more suitable tool for checking model Fermi surfaces derived by other means, than actually constructing the Fermi surface of a metal.

### Cyclotron Resonance

Let us first consider the phenomenon for the case of a classical electron. If the electron is subjected to an electromagnetic field of electric component  $\vec{E}$  and magnetic components  $\vec{H}$ , then the force on the electron is given by

$$\vec{F} = e(\vec{E} + \frac{1}{c} \vec{v} \times \vec{H}) \quad (3.14)$$

where  $\vec{v}$  is the electron velocity. The total energy  $E$ , then, absorbed by the electron is given by

$$E(t) = \int_0^t \vec{F}(t) \cdot \vec{v}(t) dt \quad (3.15)$$

and



$$\frac{d\bar{E}}{dt} = \bar{E} \cdot \bar{v} = e\bar{v} \cdot \bar{E} \quad (3.16)$$

since  $\bar{v} \cdot \bar{H} \cdot \bar{v}$  is zero.

The equations of motion of the electron are given by setting the right hand side of (3.14) equal to  $m\bar{v}$ . If  $\bar{E}$  is circularly polarized in the x-y plane, that is

$$\begin{aligned} E_x &= E_0 \cos(\omega t + \phi) \\ E_y &= E_0 \sin(\omega t + \phi) \\ E_z &= 0, \end{aligned} \quad (3.17)$$

and if  $\bar{H}$  is of magnitude  $H_0$  in the z direction only, then the equations of motion of the electron are

$$\begin{aligned} \dot{v}_x + \Omega v_y &= \frac{\sigma}{\omega + \Omega} \cos(\omega t + \phi) \\ \dot{v}_y - \Omega v_x &= \frac{\sigma}{\omega + \Omega} \sin(\omega t + \phi) \\ \dot{v}_z &= 0 \end{aligned} \quad (3.18)$$

Here, the "cyclotron frequency"  $\Omega$  is given by

$$\Omega = eH_0/mc \quad (3.19)$$

and

$$\sigma = eE_0(\omega + \Omega)/m. \quad (3.20)$$





If  $\xi = 0$ , equations (3.18) are homogeneous, and their solutions are

$$\begin{aligned} v_x &= A \cos \Omega t + B \sin \Omega t \\ v_y &= -B \cos \Omega t + A \sin \Omega t \\ v_z &= \text{constant} \end{aligned} \quad (3.21)$$

where A and B are arbitrary, and the electron describes a circular orbit with frequency  $\Omega$  in v-space. If  $\xi \neq 0$ , particular solutions of (3.18) are given by

$$\begin{aligned} v_x &= \frac{\sigma}{\omega^2 - \Omega^2} \sin(\omega t + \varphi) - \frac{\sigma}{2\Omega} \left[ \frac{\sin(\Omega t + \varphi)}{\omega - \Omega} + \frac{\sin(\Omega t - \varphi)}{\omega + \Omega} \right] \\ v_y &= \frac{-\sigma}{\omega^2 - \Omega^2} \cos(\omega t + \varphi) + \frac{\sigma}{2\Omega} \left[ \frac{\cos(\Omega t + \varphi)}{\omega - \Omega} + \frac{\cos(\Omega t - \varphi)}{\omega + \Omega} \right]. \end{aligned} \quad (3.22)$$

If  $\omega \neq \Omega$ , equations (3.15), (3.21) and (3.22) yield

$$\begin{aligned} E(t) &= \frac{e\sigma}{2\Omega} \left[ \frac{1 - \cos(\omega - \Omega)t}{(\omega - \Omega)^2} + \frac{\cos 2\varphi - \cos((\omega - \Omega)t + 2\varphi)}{\omega^2 - \Omega^2} \right] \\ &\quad + \frac{A \sin((\omega - \Omega)t + \varphi)}{\omega - \Omega} - \frac{B [\cos \varphi - \cos((\omega - \Omega)t + \varphi)]}{\omega - \Omega}, \end{aligned} \quad (3.23)$$

and we see that the total energy absorbed by the electron is a periodic function of time.



If, on the other hand,  $\omega = \Omega$ , equation (3.23) is replaced by

$$E(t) = \frac{e}{2\Omega} \left[ \frac{t^2}{2} + \frac{\sin 2\varphi}{2\Omega} t \right] + e(A \cos \varphi - B \sin \varphi) t, \quad (3.24)$$

and in this case the energy absorbed by the electron is a quadratically increasing function of time.

Let us now assume that for some effective mass  $m^*$  (Chambers' (1956) "orbit mass"; Pippard's (1960) "cyclotron mass") that we can rewrite equation (3.14) in the form

$$\hbar \dot{\mathbf{k}} = e(\bar{\mathbf{A}} \times \bar{\mathbf{v}})/c \quad (3.28)$$

where  $\bar{\mathbf{E}}$  is now zero and  $\bar{\mathbf{v}}$  is given by

$$\hbar \bar{\mathbf{v}} = \nabla_{\mathbf{k}} E(\bar{\mathbf{k}}). \quad (3.26)$$

In rectangular coordinates (3.25) and (3.26) give

$$\begin{aligned} \hbar \dot{k}_x &= - \frac{e\hbar}{hc} \cdot \frac{\partial E}{\partial k_y} \\ \hbar \dot{k}_y &= + \frac{e\hbar}{hc} \cdot \frac{\partial E}{\partial k_x} \end{aligned} \quad (3.27)$$

and  $k_z = 0$ . If curvilinear coordinates  $k_t$  and  $k_n$  are set up in  $k$  space such that  $k_t$  is tangential and  $k_n$  normal to the trajectory described by equations (3.27) then these equations imply that

$$\hbar \dot{k}_t = \frac{e\hbar}{hc} \frac{dE}{dk_n} \quad (3.28)$$



since  $\partial E / \partial k_t = 0$ , where we have taken  $\partial(k_t, k_n) / \partial(k_x, k_y)$  to have magnitude unity.

Equation (3.28) may be rewritten as

$$dt = \frac{\hbar^2 c}{eH} \frac{dk_n}{dE} dk_t, \quad (3.29)$$

and therefore if the trajectory in  $k$ -space is closed, the orbit time  $\tau$  is given by

$$\tau = \frac{\hbar^2 c}{eH} \oint \frac{dk_n}{dE} dk_t. \quad (3.30)$$

But

$$\oint (dk_n) dk_t = dA \quad (3.31)$$

where  $A$  is the area enclosed (in  $k$ -space) by the orbit, and so

$$\tau = \frac{\hbar^2 c}{eH} \frac{dA}{dE}. \quad (3.32)$$

The cyclotron frequency  $\Omega$ , may then be written as

$$\Omega = \frac{2\pi}{\tau} = \frac{eH}{m^* c} \quad (3.33)$$

where

$$m^* = \frac{\hbar^2}{2\pi} \frac{dA}{dE}. \quad (3.34)$$

If, now, we assume that for small  $H$  we can neglect the quantization of  $E$  and  $A$  and write





$$E = \hbar^2 k^2 / 2m \quad (3.35)$$

and

$$A = \pi k^2 \quad (3.36)$$

for an otherwise free electron, then

$$\frac{dA}{dE} = \frac{2\pi m}{\hbar^2} \quad (3.37)$$

and

$$m = m^* \quad (3.38)$$

as expected.

If, however,  $E$  and  $A$  are more complicated functions of  $\vec{k}$ , then measurements of  $\Omega$ , the frequency at which resonant absorption of energy occurs upon application of a circularly polarized electric field, provides  $m^*$  from equation (3.33), and thus  $dA/dE$  with the aid of (3.34).

Now,  $m^*$  depends on both  $E$  and  $k_z$ , but since only those electrons near the Fermi surface are able to absorb energy, any  $m^*$  measured will be approximately  $m^*(E_f, k_z)$ . The procedure described, however, provides no means of singling out a particular  $k_z$ , and so the measured  $m^*$  will be an average value over  $k_z$  of  $m^*(E_f, k_z)$ .

Chambers (1956) has pointed out that if the applied magnetic field is almost parallel to the surface of the metal, then only those electrons for which  $v_z$  in the direction of



the field is zero, or very small, will return to the same place in the surface layer and thus be able to resonate. In this fashion one should be able to measure  $m^*$  for a localized group of electrons, rather than obtaining an average of  $m^*$  for the whole Fermi surface.

### The de Haas-van Alphen Effect

During experiments concerning the magnetic susceptibility of single bismuth crystals at low temperatures, de Haas and van Alphen (1930) discovered that the susceptibility varied in an unusual oscillatory fashion with the applied magnetic field. Following the treatments given by Shoenberg (1957) and Chambers (1956) the origin of the effect may be determined in the manner outlined below.

Given an electron traveling on a curve on a surface of constant energy in  $k$ -space, the application of a constant magnetic field will alter the orbit in  $k$ -space to allow only those orbits corresponding to the permissible energy levels,  $E_n$ . It has been shown by Onsager (1952) that if the field is in the direction, then the allowed orbits in  $k$ -space are those for which  $A$ , the area of the projection of the orbit on the  $k_x - k_y$  plane, is given by

$$A = (n + \gamma) 2\pi e \hbar / mc$$

where  $n$  is an integer and  $\gamma$  is an undetermined phase factor. The value  $\gamma = 1/2$  gives the correct energy for an empty lattice.

For an infinite empty lattice, then, the Fermi surface, upon application of a magnetic field in the  $z$  direction, becomes a discrete set of cylinders of circular cross-section, with  $k_z$  as their axes. Each of the quantized states is now



of sufficient degeneracy that the total number of states previously available in the sphere is now available on the cylinders (Pippard (1960)). For a non-empty lattice the Fermi volume will be broken up not into circular cylinders, but into tubes of variable cross-section which may be inclined to the  $k_z$  direction.

The total energy  $W$ , of the electrons in such situation is given by

$$\begin{aligned}
 W &= \int_{-\infty}^{\infty} \sum \left[ \frac{2\pi e \mathcal{H}}{\hbar c} \right] E_n(\mathcal{H}, k_z) \left[ \frac{2v dk_z}{(2\pi)^3} \right] \\
 &= \frac{e \mathcal{H} v}{2\pi^2 \hbar c} \int_{-\infty}^{\infty} \sum_n E_n(\mathcal{H}, k_z) dk_z. \quad (3.40)
 \end{aligned}$$

Here  $v$  is the volume of the metal,  $E_n$  the energy of the  $n$ 'th permitted state given  $\mathcal{H}$  and  $k_z$ , and  $2\pi e \mathcal{H} / \hbar c$ , the area between permitted orbits, times  $2v dk_z / (2\pi)^3$  gives the number of states at  $\mathcal{H}$ ,  $k_z$ . The upper limit of the summation need only be taken as the largest  $n$  for which  $E_n(\mathcal{H}, k_z) < E_F$ , the Fermi energy.  $n$ , of course, depends on  $k_z$ , and we assume here that  $E_F$  is independent of  $\mathcal{H}$ , which is approximately true except for very high values of  $\mathcal{H}$ .

Thus, as  $\mathcal{H}$  increases, a term drops out of the integrand of equation (3.40) whenever  $E_n(\mathcal{H}, k_z)$  grows to  $E_F$ , or in other words, whenever  $A_n(E_n, \mathcal{H}, k_z)$  grows to  $A(E_F, 0, k_z)$ . Let us assume now that  $\mathcal{H} = \mathcal{H}'$  makes  $A_j$  equal to  $A(E_F, 0, k_z)$ . From equation (3.39)

$$A_j(E_j, \mathcal{H}', k_z) = (j+\gamma) 2\pi e \mathcal{H}' / \hbar c. \quad (3.41)$$





Let us also assume that increasing  $\hbar$  from  $\hbar'$  to  $\hbar''$  makes  $A_{j-1}$  equal to  $A(E_F, 0, k_z)$ . Then

$$A_{j-1}(E_{j-1}, \hbar'', k_z) = \left( \frac{\hbar''}{\hbar'} - 1 \right) \hbar' / 2c \quad (3.41)$$

since the left hand sides of (3.41) and (3.42) are both equal to  $A(E_F, 0, k_z)$ , we find that

$$\Delta = \frac{1}{\hbar'} - \frac{1}{\hbar''} = \frac{2\pi e}{\hbar c A(E_F, 0, k_z)} \quad (3.43)$$

The integrand of equation (3.40), then has discontinuities spaced  $\Delta$  apart in  $1/\hbar$ , that is, the integrand is an oscillatory function of  $1/\hbar$ , with "period"  $2\pi e / \hbar c A(E_F, 0, k_z)$ .

Now, as  $\hbar$  increases, the "tubes" in  $k$ -space containing the permissible orbits will expand according to equation (3.39). It is clear that the expansion of most of the tubes can vary  $W$  only smoothly. There are only two conditions for which the expansion of a tube can cause a discontinuity in the integrand of  $W$ : those tubes for which the permissible range  $k_z$  (determined by  $E_F$ ) is so small that any increase in  $\hbar$  (and therefore  $A$ ) causes it to vanish, and those tubes which are tangent to the Fermi surface at some point, so that any increase in  $A$  causes the tube to split into an upper and lower tube. For convex Fermi surfaces only the first condition applies and therefore only that values of  $k_z$  for which  $A(E_F, 0, k_z)$  is a maximum will cause discontinuities in the integrand of  $W$  as  $\hbar$  increases. For Fermi surfaces which are not convex, or even of one sheet, all the values of  $k_z$  for which  $A(E_F, 0, k_z)$  is a maximum or a minimum will cause discontinuities in the integrand of equation (3.40). (See figure 5).

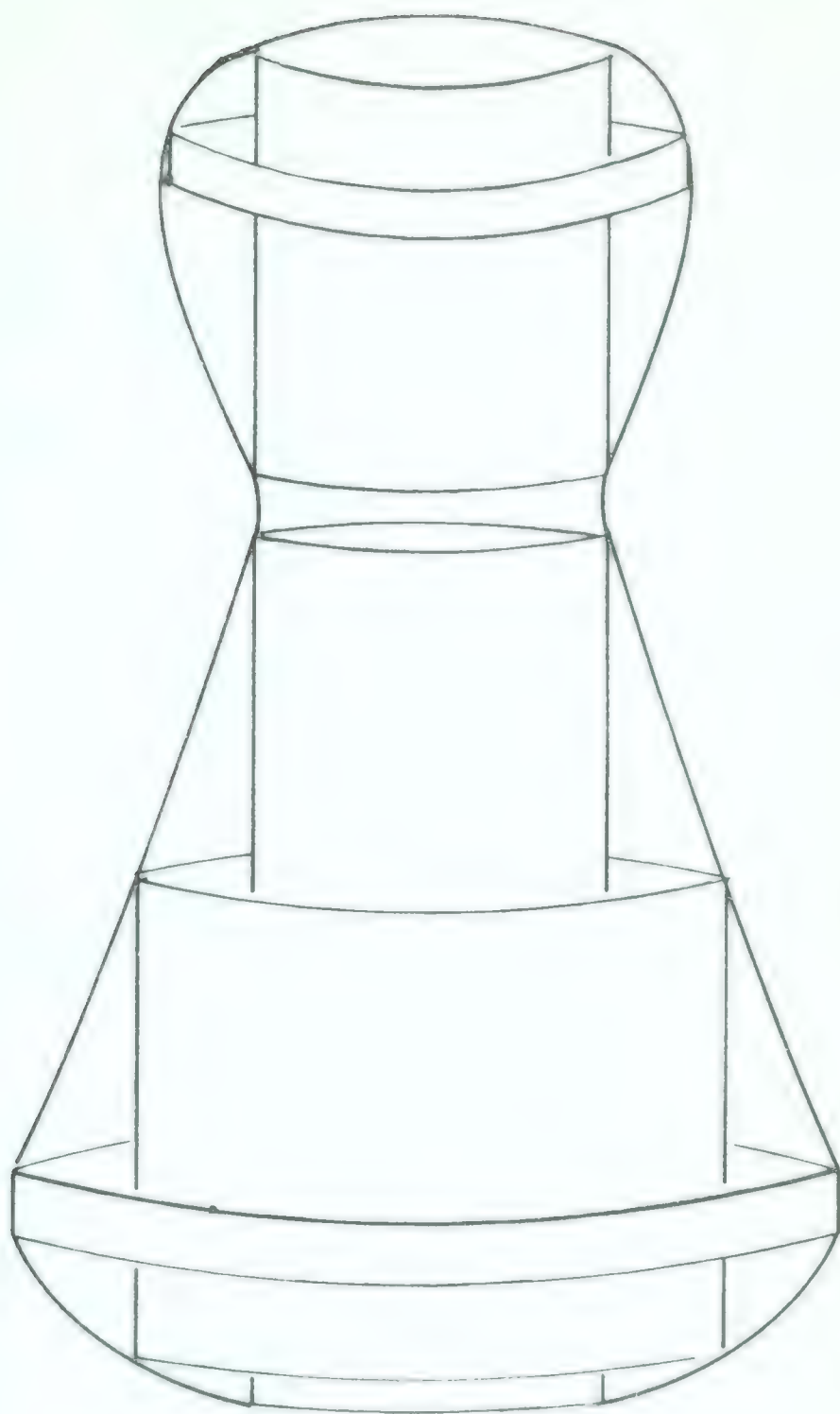


## FIGURE 5

## The de Haas-van Alphen Effect

The two cylinders at the local maxima of the cross sectional area will disappear with increasing magnetic field. The minimum in the cross sectional area of the Fermi surface has just caused one cylinder to break into two.









If we now call one of these extremal cross-sectional areas of the Fermi surface  $A'$ , we see that  $W$ , and therefore  $\chi = -\partial^2 W / \partial H^2$ , will oscillate with period  $\Delta$  in  $1/H$  given by

$$\Delta = 2\pi e / \hbar c A'. \quad (3.44)$$

One must point out that if several cross-sectional extremes of the Fermi surface exist for a given crystal orientation, then  $\chi$  will oscillate with several periods, and a complicated beat structure in  $\chi(1/H)$  may result.

We note here that the difference  $\Delta E$  between  $E_j$  and  $E_{j-1}$ , when  $A$  is near  $A'$ , is approximately given by

$$\Delta E = \frac{dE(A')}{dA} \Delta A = \frac{2\pi e \hbar}{\hbar c} \frac{dE(A')}{dA} = \frac{e \hbar \hbar}{m^*(A') c}, \quad (3.45)$$

where  $m^*$  is the "orbit mass" encountered in cyclotron resonance, given by equation (3.34). And since  $\Omega$ , the cyclotron frequency is given by

$$\Omega = \frac{e \hbar}{m^* c} \quad (3.46)$$

then

$$\Delta E = \hbar \Omega.$$

that is, the cyclotron frequency  $\Omega$  is simply that frequency which provides the appropriate amount of energy  $\Delta E$  for transitions between adjacent quantized orbits.

In the above analysis we have implicitly assumed that the temperature  $T$  was zero. If  $T$  is not zero, but large enough such that  $kT \sim \Delta E$ , the energy difference between successive



quantized orbits, then, as the cross-sectional area  $A$  of an orbit increases with  $H$  through a somewhat fuzzy Fermi surface, the change in the integrand of  $W$  (from equation (3.40)) will no longer be discontinuous, but will still be marked if  $T$  is small enough. The period, then, of  $W$  will be unaffected, but the amplitude of the oscillations will be reduced. One expects, then, that the amplitude of the oscillations of  $\chi$  (which is equal to  $-\partial^2 F / \partial H^2$  for  $T \neq 0$ , where  $F$  is the free energy) to depend on

$$\frac{kT}{\Delta E} = \frac{kTm^*(A')c}{eH\hbar} \quad (3.47)$$

when  $T \neq 0$ . Lifshitz and Kosevich (1954, 1955) have shown that this indeed is the case; they find for the oscillatory term in  $F$

$$F_{\text{osc}} \propto T H^{3/2} \cos[\pi c A' / eH + \delta] \exp[-2\pi^2 kTm^*(A')c / eH\hbar] \quad (3.48)$$

Thus for various orientations of the magnetic field one can find from measurements of the period in  $1/H$  of  $\chi$ , the extreme cross-sections  $A'$  of the Fermi surface, and from amplitude measurements one can find  $m^*(A')$ , that is  $dA'/dE$ . We note that  $m^*(A')$  from equation (3.48) is the effective mass for a particular  $k$ -space orbit, rather than an average value from several orbits.



## CHAPTER IV

### STANDARD METHODS FOR CALCULATING ELECTRONIC ENERGY BANDS

In this chapter we examine briefly some of the more widely used procedures for determining  $(E, \bar{k})$  relationships. The methods considered can be classified roughly into three groups: cellular methods, tight binding methods, and plane wave methods; and this is the order in which they have been presented. The classification, however, is far from unique, since many of the procedures contain aspects from more than one of the main groups.

In addition to individual references to them, extensive use has been made of the review articles written by Reitz (1955) and Pincherle (1960).

#### The Wigner-Seitz Cellular Method

The cellular procedure described below was first suggested by Wigner and Seitz (1933, 1934). With this method the crystal is divided up into the most symmetric unit cells, commonly referred to as Wigner-Seitz cells, and inside each of these cells the crystal potential is approximated to by a potential which is spherically symmetric.

Using this approximate potential the Schrodinger equation is now separable, and the solutions to the angular parts are, of course, the spherical harmonics  $Y_{\ell}^m(\theta, \phi)$ . The radial solution  $f_{\ell}(r, E_{\bar{k}})$  satisfies the differential equation

$$f_{\ell}'' + (E_{\bar{k}} - V(r) - \ell(\ell+1)/r^2)f_{\ell} = 0, \quad (4.1)$$





and so

$$\psi_{\vec{k}}^-(\vec{r}) = \sum_{\ell, m} a_{\ell m} Y_{\ell}^m(\theta, \varphi) f_{\ell}(r, E_{\vec{k}}^-) / r. \quad (4.2)$$

The solution (4.2) is, of course, valid only in the cell centered at  $\vec{r} = \vec{0}$ , but similar solutions  $\psi_{\vec{k}}^-(\vec{r} - \vec{R}_i)$  are valid in cells centered about the lattice points given by  $\vec{R}_i$ .

In principle, the procedure would be to determine the boundary conditions that  $\psi$  must satisfy on the surface of a Wigner-Seitz cell by means of the Bloch condition

$$\psi_{\vec{k}}^-(\vec{r} + \vec{R}_i) = e^{i\vec{k} \cdot \vec{R}_i} \psi_{\vec{k}}^-(\vec{r}); \quad (4.3)$$

these boundary conditions would then be used to determine the  $a_{\ell m}$  in (4.2), and, as usual, one would find that only for a discrete set of  $E_{\vec{k}}^-$ 's, given  $\vec{k}$ , could one find non-trivial solutions for the  $a_{\ell m}$ .

The boundary conditions are easily determined as follows. Let  $\vec{R}$  be a lattice vector corresponding to the center of a nearest neighbour cell to the cell under consideration (centered at  $\vec{r} = \vec{0}$ ). Let  $\vec{r}_1$  define a point on the face between these two cells, and let  $\vec{r}_2$  define a corresponding point on the opposite face of the zero centered cell such that  $\vec{r}_2 = \vec{r}_1 - \vec{R}$ . Let  $\vec{\epsilon}$  be an infinitesimal vector in the direction of  $\vec{R}$  so that  $\vec{r}_1 - \vec{\epsilon}$  is inside the zero centered cell, while  $\vec{r}_1 + \vec{\epsilon}$  is inside the neighbouring cell. For continuity of  $\psi$  we require that

$$\psi_{\vec{k}}^-(\vec{r}_1 - \vec{\epsilon}) = \psi_{\vec{k}}^-(\vec{r}_1 + \vec{\epsilon}), \quad (4.4)$$



but  $\bar{r}_1 + \bar{\epsilon} = \bar{r}_2 + \bar{R} + \bar{\epsilon}$ , and so

$$\psi_{\bar{k}}(\bar{r}_1 - \bar{\epsilon}) = \psi_{\bar{k}}(\bar{r}_2 + \bar{R} + \bar{\epsilon}) = e^{i\bar{k} \cdot \bar{R}} \psi_{\bar{k}}(\bar{r}_2 + \bar{\epsilon}), \quad (4.5)$$

and as  $\bar{\epsilon} \rightarrow \bar{0}$  we find

$$\psi_{\bar{k}}(\bar{r}_1) = e^{i\bar{k} \cdot \bar{R}} \psi_{\bar{k}}(\bar{r}_2). \quad (4.6)$$

Similarly, for continuity of  $\nabla\psi$  we require that

$$\frac{\partial \psi_{\bar{k}}(\bar{r}_1 - \bar{\epsilon})}{\partial n_1} = - \frac{\partial \psi_{\bar{k}}(\bar{r}_1 + \bar{\epsilon})}{\partial n_2} = - e^{i\bar{k} \cdot \bar{R}} \frac{\partial \psi(\bar{r}_2 + \bar{\epsilon})}{\partial n_2} \quad (4.7)$$

where  $n_1$  and  $n_2$  respectively denote the outward normals on the mutual face of the zero centered and neighbouring cells. As  $\bar{\epsilon} \rightarrow \bar{0}$  we obtain

$$\frac{\partial \psi(\bar{r}_1)}{\partial n_1} = - e^{i\bar{k} \cdot \bar{R}} \frac{\partial \psi(\bar{r}_2)}{\partial n_2}. \quad (4.8)$$

In principle the boundary conditions (4.6) and (4.8) should be applied to  $\psi$  to determine the  $E_{\bar{k}}$  and the coefficients  $a_{\bar{k}m}$  in the expansion (4.2). In practice the computational difficulties arising are prohibitive, and Wigner and Seitz (1933, 1934) made the following approximations.

They used this procedure for  $\bar{k} = \bar{0}$ , and retained only the first term in the series expansion (4.2). The wave function, then is given by

$$\psi_{\bar{k}}(\bar{r}) \equiv \psi_{\bar{k}}(\bar{r}) = F(\bar{r}) \quad (4.9)$$



where  $F(r) = a_{\circ\circ} f_{\circ}(r, E_{\bar{k}})/r$ .

The boundary condition (4.6) is now automatically satisfied, since  $\bar{k} = \bar{0}$  and  $\psi$  is a function only of the length of the radius vector,  $r$ . The Wigner-Seitz cell was then replaced by a sphere of radius  $r_{\circ}$  and volume  $v$ , equal in volume to the unit polyhedron, and the remaining boundary condition applied to this sphere. In this case equation (4.8) implies that

$$\frac{\partial F(r_{\circ})}{\partial r} = 0. \quad (4.10)$$

For non-zero values of  $\bar{k}$ , Bardeen (1938) constructed a procedure to find the eigenvalues of other states by means of perturbation theory. The wave function is written in the Bloch form  $e^{i\bar{k} \cdot \bar{r}} u(\bar{r})$  and substituted into Schrodinger's equation to get the differential equation satisfied by  $u(\bar{r})$ . The term in  $\bar{k} \nabla u$  in this equation is then treated as a perturbation. The method involves expanding  $u(\bar{r})$  and  $E$  as power series in  $\bar{k}$ , and it is shown that

$$E_{\bar{k}} = E_{\circ} + \alpha |\bar{k}|^2 + O(|\bar{k}|^4), \quad (4.11)$$

where

$$\alpha = \gamma [(r/P)(dP/dr) - 1]_{r_{\circ}}, \quad (4.12)$$

$$\gamma = (4\pi/3) r_{\circ}^3 [\psi(r_{\circ})]^2, \quad (4.13)$$

and where  $P$  is a solution vanishing at the origin to

$$P'' + (E_{\circ} - V - 2/r^2)P = 0. \quad (4.14)$$





Equation(4.11) is of course valid only when the expression  $\bar{k}\nabla u$  is small, and this is the case, in general, only for small  $|\bar{k}|$ .

### The Expansion of $\psi$ in Lattice Harmonics

This method, developed by Slater (1934a, 1934b) and Von der Lage and Bethe (1947) is essentially a modification of the Wigner-Seitz cellular method.

The crystal potential inside one Wigner-Seitz cell is assumed to be spherically symmetric, in which case equations (4.1) and (4.2) apply.

$$f_{\ell}'' + (E_{\bar{k}} - V(r) - \ell(\ell+1)/r^2)f_{\ell} = 0, \quad (4.1)$$

$$\psi_{\bar{k}}(\bar{r}) = \sum_{\ell, m} a_{\ell m} Y_{\ell}^m(\theta, \varphi) f_{\ell}(r, E_{\bar{k}})/r. \quad (4.2)$$

It was suggested by Slater that instead of approximating to the Wigner-Seitz cell by a sphere of equal volume in order to permit the convenient application of the boundary conditions, that instead one limit the number of  $\ell$ 's used in the expansion (4.2), and then apply the boundary conditions at a number of specific points on the surface of the Wigner-Seitz cell itself.

It was found, however, that the resulting values  $E(\bar{k})$  were quite sensitive to the positions on the unit cell at which the boundary conditions were applied, unless the maximum  $\ell$  used was quite large. For this reason only points  $\bar{k}$  possessing a high degree of symmetry in the first Brillouin zone should be considered with this method, since for these values of  $\bar{k}$  many of the spherical harmonics are of unsuitable symmetry. This, of course, implies that their coefficients must be zero,



thus permitting one to use a fairly large  $\ell$  and still have only a reasonable number of terms in the expansion (4.2).

A further improvement was made by Von der Lage and Bethe (1947), by rewriting the expansion (4.2) in the form

$$\psi_{\bar{k},s} = \sum_{\ell,m} b_{\ell t} K_{s,\ell t}(\theta,\varphi) f_{\ell}(r, E_{\bar{k}})/r. \quad (4.15)$$

Here  $K_{s,\ell t}(\theta,\varphi)$  is a "lattice harmonic", or Kubic harmonic" for lattices having cubic symmetry.  $K_{s,\ell t}(\theta,\varphi)$  is a linear combination of the spherical harmonics  $Y_{\ell}^m(\theta,\varphi)$  which transforms according to the irreducible representation labeled  $s$  of the appropriate subgroup (dictated by  $\bar{k}$ ) of the point group of the lattice. There may of course be more than one such linear combination for a given  $\ell$ , hence the subscript  $t$ . The lattice harmonics are independent of the crystal potential and to some extent, of the lattice itself, and therefore having once been found, they can be used with a variety of potentials in crystals having the same symmetry properties.

Von der Lage and Bethe tabulated Kubic harmonics for the full cubic group. These apply for  $\bar{k} = \pi/a(1,0,0)$  in body centered cubic lattices, for  $\bar{k} = \pi/a(1,1,1)$  in simple cubic lattices, and  $\bar{k} = \bar{0}$  in cubic lattices, simple, body centered, or face centered. Howarth and Jones (1952) have tabulated kubic harmonics for other symmetry points, and Bell (1954) has given lattice harmonics for various structures.

The use of lattice harmonics reduces considerably the number of terms for a given  $\ell$  in the expansion of  $\psi$ . The boundary conditions are now applied at selected points on opposite faces of the Wigner-Seitz cell to determine which



values of  $E_{\vec{k}}$  permit non-trivial solutions for the coefficients  $b_{\vec{k}t}$ .

Altman (1958) has given an alternate procedure for applying the boundary conditions. Instead of picking just enough points on the boundary of the Wigner-Seitz cell to determine the  $b_{\vec{k}t}$ , the procedure is to pick some large number  $N$ , of points on the boundary of the cell, and then minimize the sum of the squares of the errors for each boundary condition, for each point, that is, a least squares technique. The procedure then reduces to the solution of a matrix eigenvalue problem.

#### Linear Combination of Atomic Orbitals; Tight Binding

The following method was first proposed by Bloch (1928) and comprises an attempt to approximate to a crystal wave function by a linear combination of atomic orbitals.

It is assumed that the atomic orbital  $\chi_n(\vec{r})$  satisfies the equation

$$-\nabla^2 \chi_n + W \chi_n = E_n^0 \chi_n, \quad (4.16)$$

and also that we can write the crystal basis function  $\psi_{\vec{k}n}(\vec{r})$  in the form

$$\psi_{\vec{k}n}(\vec{r}) = \sum_j e^{i\vec{k} \cdot \vec{R}_j} \chi_{nj}(\vec{r}) \quad (4.17)$$

where

$$\chi_{nj}(\vec{r}) \equiv \chi_n(\vec{r} - \vec{R}_j) \quad (4.18)$$

The  $\vec{R}_j$  are, of course, lattice vectors.







We note here that  $\psi_{\bar{k}n}$  is in the Bloch form, since we may rewrite equation (4.17) in the form

$$\psi_{\bar{k}n}(\bar{r}) = e^{i\bar{k} \cdot \bar{r}} \sum_j e^{i\bar{k} \cdot (\bar{R}_j - \bar{r})} \chi_n(\bar{r} - \bar{R}_j) \quad (4.19)$$

where the factor involving the sum over  $j$  clearly has the period of the lattice for an infinite crystal.

We now assume that the crystal wave function  $\psi_{\bar{k}}(\bar{r})$  is given by

$$\psi_{\bar{k}}(\bar{r}) = \sum_n A_n \psi_{\bar{k}n}(\bar{r}) \quad (4.20)$$

where the sum over  $n$  is to be taken over the number of degenerate states of the atomic level  $E_n^\circ$ . Substituting (4.20) into

$$-\nabla^2 \psi_{\bar{k}} + V(\bar{r}) \psi_{\bar{k}} = E_{\bar{k}} \psi_{\bar{k}} \quad (4.21)$$

where  $V(\bar{r})$  is the crystal potential, we get

$$\sum_n A_n (\nabla^2 \psi_{\bar{k}n} + (E - V) \psi_{\bar{k}n}) = 0. \quad (4.22)$$

But

$$\nabla^2 \psi_{\bar{k}n} = \sum_j e^{i\bar{k} \cdot \bar{R}_j} \nabla^2 \chi_{nj}, \quad (4.23)$$

which, using equation (4.16) becomes

$$\nabla^2 \psi_{\bar{k}n} = \sum_j e^{i\bar{k} \cdot \bar{R}_j} (W_j - E_n^\circ) \chi_{nj} \quad (4.24)$$



where

$$W_j(\bar{r}) \equiv W(\bar{r} - \bar{R}_j). \quad (4.25)$$

Then, substituting (4.17) and (4.24) into equation (4.22) we get

$$\sum_n A_n \left[ \sum_j e^{i\bar{k} \cdot \bar{R}_j} (W_j - V + E_{\bar{k}} - E_n^0) \chi_{nj} \right] = 0. \quad (4.26)$$

We will now multiply this result by  $\chi_{mi}^*$  and integrate over all space. We assume here that the  $\chi_{nj}$ ,  $n=1,2,3,\dots$  form an orthonormal set, and also that the "overlap" integrals may be neglected; this is, for this calculation we assume that

$$\int \chi_{mi}^* \chi_{nj} d\tau = \delta_{mn} \delta_{ij}. \quad (4.27)$$

Equation (4.26) now yields

$$\sum_n A_n \left[ (E_{\bar{k}} - E_n^0) \delta_{mn} + \sum_j e^{i\bar{k} \cdot (\bar{R}_j - \bar{R}_i)} \int \chi_{mi}^* (W_j - V) \chi_{nj} d\tau \right] = 0. \quad (4.28)$$

Since we are summing over  $j$ , the left side of (4.28) is independent of  $i$ ; we will drop the subscript, then, to get

$$\sum_n A_n \left[ (E_{\bar{k}} - E_n^0) \delta_{mn} + \sum_j e^{i\bar{k} \cdot \bar{R}_j} \int \chi_m^* (W_j - V) \chi_{nj} d\tau \right] = 0. \quad (4.29)$$

For a non-degenerate  $s$  level the sum over  $n$  contains only one term; only the value  $m = n$  need be used then, and we find



that

$$E_{\bar{k}} = E_n^{\circ} - \sum_j e^{i\bar{k} \cdot \bar{R}_j} \int \chi_n^* (W_j - V) \chi_{nj} d\tau \quad (4.30)$$

as an explicit dispersion relationship.

On the other hand, for a triply degenerate p state the sum over n contains three terms  $n = n_1, n_2, n_3$ ; we must therefore also use equation (4.29) with  $m = n_1, n_2, n_3$ . The condition in this case for non-trivial solutions  $A_n$  is the vanishing of the determinant of coefficients, each coefficient being given by the term in square brackets in (4.29). This condition, then, provides an implicit relation between E and  $\bar{k}$ .

The matrix elements (coefficients of  $A_n$ ) in (4.29) may be evaluated to varying degrees of accuracy. In this approximation, since it was assumed that the atomic orbitals  $\chi$  centered at different lattice points overlap only slightly, it is consistent also to assume that the sum over j in (4.29) need be taken over nearest neighbours only.

If the assumption that the atomic orbitals centered at different lattice points do not overlap is dropped, and if the overlap integrals are included in the calculation, then the sum over j in (4.29) may reasonably be extended to include neighbours other than nearest until the matrix elements converge.

To do this equation (4.27) is replaced by

$$\int \chi_{mi}^* \chi_{ni} d\tau = \delta_{mn}, \text{ all } i \quad (4.31)$$

and

$$S_{mn}(ij) = \int \chi_{mi}^* \chi_{nj} d\tau = \delta_{ij}. \quad (4.32)$$

If we now multiply equation (4.26) by  $\chi_{mi}^*$  and integrate over





all space we find

$$\sum_n A_n \left[ (E_k - E_n^0) \left[ 1 + \sum_j e^{i\vec{k} \cdot (\vec{R}_j - \vec{R}_i)} S_{mn}(ij) \right] + \sum_j e^{i\vec{k} \cdot (\vec{R}_j - \vec{R}_i)} \int \chi_{mi}^*(W_j - V) \chi_{mj} d\tau \right] = 0, \quad (4.33)$$

and again, since we sum over  $j$  we may set  $i = 0$  and neglect the subscript to get

$$\sum_n A_n \left[ (E_k - E_n^0) \left( 1 + \sum_j e^{i\vec{k} \cdot \vec{R}_j} S_{mn}(0j) \right) + \sum_j e^{i\vec{k} \cdot \vec{R}_j} \int \chi_m^*(W_j - V) \chi_{nj} d\tau \right] = 0 \quad (4.34)$$

A non-degenerate state now yields

$$E_{\vec{k}} = E_n^0 - \frac{\sum_j e^{i\vec{k} \cdot \vec{R}_j} \int \chi_m^*(W_j - V) \chi_{mj} d\tau}{1 + \sum_j e^{i\vec{k} \cdot \vec{R}_j} S_{mn}(0j)} \quad (4.35)$$

and a degenerate state will again result in an implicit dispersion relation in the form of a determinant set equal to zero. The sum over  $j$ , now, need no longer be restricted to nearest neighbours.



### Orthogonalized Atomic Orbitals

Lowdin (1950) suggested a somewhat different procedure for extending the tight binding method of finding dispersion relations. The procedure consists of replacing the atomic orbitals  $\chi_{ni}(\bar{r})$  by an appropriate linear combination  $\varphi_{ni}(\bar{r})$  of the form

$$\varphi_{ni}(\bar{r}) + \sum_j \alpha_{ij} \chi_{nj}(\bar{r}). \quad (4.36)$$

The coefficients  $\alpha_{ij}$  are chosen such that if the  $\chi_{ni}$  form an orthogonal set on the subscript  $n$  (which refers to different atomic energy levels at a given lattice position), then the  $\varphi_{ni}$  will form an orthogonal set on both  $n$  and  $i$ , that is

$$\int \varphi_{ni}^*(\bar{r}) \varphi_{mj}(\bar{r}) d\tau = \delta_{mn} \delta_{ij}. \quad (4.37)$$

Lowdin showed that

$$\alpha_{ij} = [ (1+S)^{-1/2} ]_{ji} \quad (4.38)$$

where the elements of the matrix  $S$  are given by the overlap integrals for a given level of the atomic energy  $E_n^0$ ; thus

$$S_{ij}^{(n)} = \int \chi_{ni}^* \chi_{nj} d\tau - \delta_{ij}. \quad (4.39)$$

The matrix  $(1+S)^{-1/2}$  is defined by the expansion

$$(1+S)^{-1/2} = I - (1/2)S + (3/8)S^2 - (5/16)S^3 + \dots, \quad (4.40)$$



and therefore

$$\begin{aligned} \alpha_{ij} = & \delta_{ji} - (1/2)S_{ji} + (3/8) \sum_n S_{jn} S_{ni} \\ & + (5/16) \sum_n \sum_m S_{jn} S_{nm} S_{mi} + \dots \end{aligned} \quad (4.41)$$

Since the  $\chi$ 's are atomic orbitals which are at least reasonably localized near a given lattice point, the expansion (4.41) should converge quickly to give the necessary coefficients  $\alpha_{ij}$ . A knowledge of the  $\alpha_{ij}$  permits the construction of the orthogonalized atomic orbitals  $\phi_{ni}$  from equation (4.36), and these functions are then used in place of the  $\chi_{ni}$  in the formalism of the tight binding method. Slater and Koster (1954) proved that the Lowdin functions  $\phi_{ni}$  have symmetry properties corresponding to the atomic orbitals from which they were derived. An s state, then still leads to an explicit dispersion relation, and in general the order of the secular equation supplying the  $(E, \bar{k})$  relation is the same whether one uses atomic or orthogonalized atomic orbitals.

One requires, of course, the elements of the matrix  $(1+S)^{-1/2}$ ; a general procedure for finding these has been given by Lowdin (1951).

We note here that in order to increase the effectiveness of both the tight binding and orthogonalized atomic orbitals procedures, one could extend the sum

$$\psi_{\bar{k}}(\bar{r}) = \sum_n A_n \psi_{\bar{k}n}(\bar{r}) \quad (4.20)$$

to include terms of different energies. One could then use





a variational technique to determine the energy for a given  $\bar{k}$ .

### Linear Combination of Atomic Orbitals - Interpolation Procedure

In the two preceding sections we have seen that when the crystal orbital  $\psi_{\bar{k}}$  is approximated to by a linear combination of atomic orbitals one is led to insist that a determinant involving  $E$  and  $\bar{k}$  be zero in order that not all the coefficients in the expansion for  $\psi_{\bar{k}}(\bar{r})$  be zero. Equations (4.29) for the appropriate values of  $m$  may be rewritten as

$$|M(\bar{k}) - E_{\bar{k}} I| = 0, \quad (4.42)$$

where

$$M_{mn}(\bar{k}) = E_n^0 \delta_{mn} - \sum_j e^{i\bar{k} \cdot \bar{R}_j} \int \chi_m^* (W_j - V) \chi_{nj} d\tau. \quad (4.43)$$

Slater and Koster (1954) suggested that equation (4.42) could be used as an interpolation aid rather than as a dispersion relation. In this procedure one would treat the quantities  $E_n^0$  and  $\alpha_{nmj}$  defined by

$$\alpha_{nmj} \equiv \int \chi_m^* (W_j - V) \chi_{nj} d\tau \quad (4.44)$$

as parameters, rather than as known constants.  $E(\bar{k}_i)$  must now be determined as accurately as possible by other methods at enough points  $\bar{k}_i$  in  $k$ -space to determine the parameters  $E_n^0$  and  $\alpha_{nmj}$ . Equation (4.42) now provides a dispersion relation which fits exactly at the predetermined points  $E(\bar{k}_i)$ .

We note here that any of the various procedures which yield dispersion relations, as opposed to isolated points in



$(E, \bar{k})$  space, could be used in the above manner to provide dispersion relations passing through points  $E(\bar{k}_i)$  found by some other method.

### Plane Wave Method

Since it is known that  $\psi_{\bar{k}}(\bar{r})$  can be written in the form

$$\psi_{\bar{k}}(\bar{r}) = e^{i\bar{k} \cdot \bar{r}} u_{\bar{k}}(\bar{r}) \quad (4.45)$$

where  $u_{\bar{k}}(\bar{r})$  has the period of the lattice, perhaps the first procedure that comes to mind is the expansion of  $u_{\bar{k}}(\bar{r})$  in a series of plane waves. If this is done, then  $\psi_{\bar{k}}(\bar{r})$  may be written as

$$\psi_{\bar{k}}(\bar{r}) = \sum_{\bar{i}} C(\bar{k} + \bar{k}_i) e^{i(\bar{k} + \bar{k}_i) \cdot \bar{r}}, \quad (4.46)$$

where  $\bar{k}_i$  is a lattice vector of the reciprocal lattice. One procedure for determining  $E_{\bar{k}}$  and the coefficients  $C(\bar{k} + \bar{k}_i)$  is given by Pincherle (1960).

We will require the orthogonality of the plane waves  $e^{i\bar{k}_i \cdot \bar{r}}$  over a Wigner-Seitz cell, and this is easily demonstrated as follows. The  $e^{i\bar{k}_i \cdot \bar{r}}$ , being solutions to the Helmholtz equation with periodic boundary conditions on the unit cell are clearly orthogonal to each other if they belong to different eigenvalues. If they belong to the same eigenvalue, the product of the two plane waves is a third solution to the Helmholtz equation, which must therefore be orthogonal to unity.

If we expand the crystal potential  $V(\bar{r})$  in a Fourier series to get

$$V(\bar{r}) = \sum_{\bar{j}} W(\bar{k}_j) e^{i\bar{k}_j \cdot \bar{r}}, \quad (4.47)$$



and substitute this along with (4.46) into Schrodinger's equation we find

$$\begin{aligned}
 & \sum_i |\bar{k} + \bar{k}_i|^2 C(\bar{k} + \bar{k}_i) e^{i(\bar{k} + \bar{k}_i) \cdot \bar{r}} \\
 & + \sum_i \sum_j C(\bar{k} + \bar{k}_i) W(\bar{k}_j) e^{i(\bar{k} + \bar{k}_i + \bar{k}_j) \cdot \bar{r}} \\
 & = E \sum_i C(\bar{k} + \bar{k}_i) e^{i(\bar{k} + \bar{k}_i) \cdot \bar{r}}.
 \end{aligned} \tag{4.48}$$

If we now multiply by  $e^{-(\bar{k} + \bar{k}_n) \cdot \bar{r}}$  and integrate over a Wigner-Seitz cell we obtain

$$\left[ |\bar{k} + \bar{k}_n|^2 - E \right] C(\bar{k} + \bar{k}_n) + \sum_i C(\bar{k} + \bar{k}_i) W(\bar{k}_n - \bar{k}_i) = 0, \tag{4.49}$$

$$n = 0, 1, 2, \dots$$

That is, for non-trivial solutions  $C(\bar{k} + \bar{k}_i)$  we required the vanishing of the determinant

$$|M - EI| = 0 \tag{4.50}$$

where

$$\begin{aligned}
 M_{ij} &= W(\bar{k}_i - \bar{k}_j), \quad i \neq j \\
 &= |\bar{k} + \bar{k}_i|^2 + W(0), \quad i = j.
 \end{aligned} \tag{4.51}$$





It is easy to show that the standard variational procedure when applied to (4.46) also leads to conditions (4.41) and (4.42) for the determination of  $E(\bar{k})$  and  $C(\bar{k}+\bar{k}_i)$ .

### Orthogonalized Plane Wave Method

The potential  $V(\bar{r})$  under consideration in Schrodinger's equation is a crystal potential which is often written in the form

$$V(\bar{r}) = \sum_i V^i(\bar{r}-\bar{R}_i) \quad (4.52)$$

where  $V^i(\bar{r})$  may be termed a "site" potential. If  $V^i$  is indeed an atomic potential, then an expansion such as (4.46) of  $\psi$  in terms of plane waves, or any other complete set of functions, must converge to the energy of the innermost core electron if enough terms are used. (See Herring (1940)). Since these are not the states with which we are concerned in energy band considerations, steps must be taken to prevent this from occurring. Herring (1940) developed the orthogonalized plane wave method to overcome this difficulty.

Briefly, the procedure consists of using as basis functions, instead of the functions  $e^{i(\bar{k}+\bar{k}_i)\cdot\bar{r}}$ , the functions

$$Y_i(\bar{k},\bar{r}) = e^{i(\bar{k}+\bar{k}_i)\cdot\bar{r}} - \sum_j \mu_{ij} \varphi_{\bar{k}+\bar{k}_i,j}(\bar{r}) \quad (4.53)$$

where

$$\varphi_{\bar{k},s} = \sum_n e^{i\bar{k}\cdot\bar{R}_n} \chi_s(\bar{r}-\bar{R}_n) \quad (4.54)$$

and



$$\mu_{ij} = \int e^{i(\bar{k} + \bar{k}_i) \cdot \bar{r}} \chi_j^*(\bar{r}) d\tau. \quad (4.55)$$

The functions  $\chi_s(\bar{r} - \bar{R}_n)$  are atomic orbitals, assumed to be orthogonal and non-overlapping, that is one assumes that

$$\int \chi_s^*(\bar{r} - \bar{R}_n) \chi_t(\bar{r} - \bar{R}_m) d\tau = \delta_{st} \delta_{nm}. \quad (4.56)$$

The crystal orbitals  $\phi_{\bar{k}s}(\bar{r})$  are the core states one wishes to avoid, and the author has shown that

$$\int Y_i^*(\bar{k}, \bar{r}) \phi_{\bar{k}'s}(\bar{r}) d\tau = 0 \quad (4.57)$$

for any values of  $\bar{k}'$  and  $s$ .

One may now set

$$\psi_{\bar{k}}(\bar{r}) = \sum_i \beta_i(\bar{k}) Y_i(\bar{k}, \bar{r}) \quad (4.58)$$

and use a variational procedure to obtain the secular equation and thence an approximate dispersion relation.

We note here that if  $V^i(\bar{r})$  in equation (4.52) is a site potential which includes the effect of the core electrons, then the plane wave expansion (4.46) for  $\psi$  will not, as contended by Pincherle (1960) converge to the wave function for the innermost core electron. However, one would still expect an expansion of  $\psi$  in terms of orthogonalized plane waves to be better than a plane wave expansion (Callaway (1958)). The plane wave expansion must rely on the potential and the variational procedure to make the final result orthogonal to the core wave functions, whereas the orthogonalized plane waves already satisfy this condition. Fewer terms in an



orthogonalized plane wave expansion should therefore be required to achieve a given level of convergence.

#### Augmented Plane Wave Method

Another procedure for constructing a suitable set of basis functions in which to expand  $\psi_{\vec{k}}(\vec{r})$  was developed by Slater (1953) and Saffren and Slater (1953). With this method the Wigner-Seitz cell is considered in two parts, one a sphere surrounding the ion at a lattice point, the second part outside this sphere but inside the unit polyhedral cell. The radius  $r_0$  of the sphere is arbitrary, except that the sphere must be contained in the unit cell.

Outside the sphere the potential is taken to be constant, and inside a spherically symmetric approximation is used. The basis functions are constructed in the following manner.

Outside the sphere every basis function is given by  $e^{i\vec{k} \cdot \vec{r}}$ . This plane wave is written in the form

$$e^{i\vec{k} \cdot \vec{r}} = \sum_{\ell} i^{\ell} (2\ell+1) P_{\ell}(\cos \theta) j_{\ell}(kr), \quad (4.59)$$

where the  $P_{\ell}(\cos \theta)$  are Legendre polynomials and the  $j_{\ell}(kr)$  are spherical Bessel functions.  $\theta$  is the angle between  $\vec{k}$  and  $\vec{r}$ .

Inside the sphere the different basis functions are given by  $u(r, \theta, E)$  for values of  $E$  yet to be determined.  $u(r, \theta, E)$  is given by

$$u(r, \theta, E) = \sum_{\ell} a_{\ell} u_{\ell}(r, E) P_{\ell}(\cos \theta) \quad (4.60)$$





where  $u_\ell(r, E)$  is the solution for a particular  $E$ , finite at the origin, of Schrodinger's equation with magnetic quantum number zero.

To make the basis functions continuous, the coefficients  $a_\ell$  are chosen to be

$$a_\ell = i^\ell (2\ell+1) j_\ell(kr_0) / u_\ell(r_0, E). \quad (4.61)$$

The derivatives, however, of the basis functions across the surface of the sphere are discontinuous.

If we now set

$$\begin{aligned} Y_{\vec{k}}(r, \theta, E) &= u(r, \theta, E), \quad 0 \leq r \leq r_0 \\ &= e^{i\vec{k} \cdot \vec{r}}, \quad r > r_0, \end{aligned} \quad (4.62)$$

then the set of basis functions is given by  $Y_{\vec{k}}(r, \theta, E_i)$ . The set of values  $(E_i)$  are chosen to be the stationary states with respect to  $E$  of

$$\langle E \rangle = \int Y_{\vec{k}}^*(r, \theta, E) H Y_{\vec{k}}(r, \theta, E) d\tau \quad (4.63)$$

It is shown by the authors that the stationary states  $E_i$  of  $\langle E \rangle$  are obtained when  $E = E_i$ , and that

$$E_i = k^2 + (4\pi r_0^2 / v) \sum_{\ell} (2\ell+1) j_\ell^2(kr_0) \frac{d}{dr} \ln u_\ell(r_0, E_i), \quad (4.64)$$

where here  $v$  is the volume of a unit cell minus the volume to the sphere of radius  $r_0$ .

Equation (4.64) must now be solved for  $E_i$ ,  $i = 1, 2, 3, \dots$  and the basis functions  $Y_{\vec{k}}(r, \theta, E_i)$  constructed and used in say, a variational procedure.



## CHAPTER V

### NEW METHODS FOR CALCULATING ELECTRONIC ENERGY

#### BANDS AND FERMI SURFACES

In this chapter we describe first a fairly standard matrix method of finding approximations to the solutions of a differential equation, and we consider in some detail the usual variational procedure. We then develop the "restricted cellular basis function" approach, which is essentially an extension of the method of "solid harmonics" suggested by Betts (1959). A second new method based on a consistency consideration is then described, and finally an interpolation scheme based on the two new procedures is considered.

#### Equivalent Matrix Equation

Variations of the procedure developed below are not uncommon; see, for example, Bickley and McNamee (1960).

Let us consider the equation

$$H\psi = \Theta \quad (5.1)$$

Where  $H$  is a linear differential operator and  $\psi$  is to satisfy the same homogeneous boundary conditions as does the given function  $\Theta$ . If we have a sufficiently complete set of basis functions  $(f_j)$  satisfying the boundary conditions of (5.1), then we may write

$$\psi = \sum_{j=1}^{\infty} a_j f_j. \quad (5.2)$$



To look for an approximate solution to equation (5.1), let us assume that we can write

$$\psi = \sum_{j=1}^{\infty} a_j f_j \quad (5.3)$$

and

$$\Theta = \sum_{j=1}^{\infty} c_j f_j. \quad (5.4)$$

The coefficients  $a_j$  in (5.3) are to be found, and the coefficients  $c_j$  in (5.4) are defined by

$$N\bar{c} = \bar{\Theta} \quad (5.5)$$

Where, of course, the  $i$ 'th component of  $\bar{c}$  is  $c_i$ , and the matrix  $N$  and the vector  $\bar{\Theta}$  are given by

$$N_{ij} = \int f_i f_j d\tau \quad (5.6)$$

and

$$(\bar{\Theta})_i = \int f_i \Theta d\tau. \quad (5.7)$$

Substituting the expansions (5.3) and (5.4) into the differential equation (5.1) yields

$$\sum_j a_j H f_j = \sum_j c_j f_j. \quad (5.8)$$

If we now multiply equation (5.8) by  $f_i$  and integrate, we get





the  $i$  th row of the matrix equation

$$H\bar{a} = N\bar{c} \quad (5.9)$$

where  $H$  is now a matrix, the elements of which are given by

$$H_{ij} = \int f_i H f_j \, d\tau \quad (5.10)$$

and the components of the vector  $\bar{a}$  are the  $a_i$ . Since we can multiply (5.8) by any  $f_i$ ,  $i=1,2,\dots,n$ , the entire matrix equation (5.9) holds.

An approximate solution to (5.1), then, is given by (5.3), where the coefficients  $a_i$  are found from

$$\bar{a} = H^{-1}N\bar{c} = H^{-1}\bar{\theta} \quad (5.11)$$

This procedure is easily modified to treat the eigenvalue equations we have been considering. If we put

$$\bar{\theta} = E\psi, \quad (5.12)$$

then it is clear that equation (5.9) is replaced by

$$H\bar{a} = EN\bar{a}. \quad (5.13)$$

The eigenvalues and eigenvectors of (5.13), then, provide approximations to the eigensolutions of the differential equation  $H\psi = E\psi$ .



### Variational Procedure

Consider the differential equation

$$H\psi = E\psi \quad (5.14)$$

plus homogeneous boundary conditions; if we multiply by  $\psi$  and integrate over the appropriate volume (5.14) leads to

$$E = \frac{\int \psi H \psi d\tau}{\int \psi^2 d\tau} . \quad (5.15)$$

It is easily demonstrated as follows that if  $H$  is Hermitian, then those functions  $\psi_n$  which produce stationary states  $E_n$  of  $E$  (as defined by (5.15)) with respect to variations in  $\psi$  are identical with the eigensolutions  $(E_n, \psi_n)$  of equation (5.14)

To do this let us expand  $\psi$  in terms of a sufficiently complete set of functions  $(f_i)$ , and then vary  $\psi$  by varying the coefficients in the expansion. Let us say, then, that  $\psi$  is given by

$$\psi = \sum_{i=1}^{\infty} a_i f_i . \quad (5.16)$$

Interchanging the order of integration and summations, substitution of (5.16) into (5.15) leads to

$$E = \frac{\sum_i \sum_j a_i a_j H_{ij}}{\sum_i \sum_j a_i a_j N_{ij}} , \quad (5.17)$$



where we again define

$$H_{ij} = \int f_i H f_j d\tau \quad (5.10)$$

and

$$N_{ij} = \int f_i f_j d\tau \quad (5.6)$$

Equation (5.17) may be written then in the form

$$E = \frac{\bar{a} \cdot (H\bar{a})}{\bar{a} \cdot (N\bar{a})} \quad (5.18)$$

Where  $H$  and  $N$  are matrices with elements  $H_{ij}$  and  $N_{ij}$  respectively. To find the stationary states of  $E$  we differentiate with respect to  $a_k$ ,  $k = 1, 2, 3, \dots$ , and insist that the results vanish.

$$\begin{aligned} \frac{\partial E}{\partial a_k} &= \sum_i a_i H_{ik} + \sum_j a_j H_{kj} \\ &- \frac{\bar{a} \cdot (H\bar{a})}{\bar{a} \cdot (N\bar{a})} \left[ \sum_i a_i N_{ik} + \sum_j a_j N_{kj} \right] = 0. \end{aligned} \quad (5.19)$$

That is

$$\frac{\partial E}{\partial a_k} = \left[ (H^T + H)\bar{a} \right]_k - \frac{\bar{a} \cdot (H\bar{a})}{\bar{a} \cdot (N\bar{a})} \left[ (N^T + N)\bar{a} \right]_k = 0 ; \quad (5.20)$$

and since this must be true for all  $k$  we find





$$(H^T + H)\bar{a} = \frac{\bar{a} \cdot (H\bar{a})}{\bar{a} \cdot (N\bar{a})} (N^T + N)\bar{a}. \quad (5.21)$$

Now,  $N$  is clearly symmetric, and so is the matrix  $H$  if the differential operator is Hermitian; with the aid of equation (5.18) then we may rewrite (5.21) in the form

$$H\bar{a} = E N\bar{a}. \quad (5.22)$$

But according to the previous section this matrix equation, where  $H$  and  $N$  are now infinite square matrices and  $\bar{a}$  is an infinite column vector, is equivalent to the differential equation  $H\psi = E\psi$  plus boundary conditions. The stationary states of (5.15), then, are the eigensolutions of (5.14) and also of (5.22).

We note here that if the differential operator is not Hermitian, then (5.22) must be replaced by

$$(1/2) (H + H^T)\bar{a} = E N\bar{a}, \quad (5.23)$$

and we have no guarantee that the eigensolutions of this equation bear any relation to those of  $H\psi = E\psi$ . If the differential operator is Hermitian, then the variational procedure leads to exactly the same result as does the equivalent matrix approach. However one important advantage, outlined below, has been gained.

To use the variational procedure as a means of finding approximate eigensolutions to  $H\psi = E\psi$ , we merely use a finite subset, say the first  $n$ , of the set of functions  $(f_i)$ , instead of using the whole set. But this is equivalent to insisting that

$$a_i = 0, \quad i = n + 1, n + 2, \dots \quad (5.24)$$



Now, from (5.18) it is clear that  $E(\bar{a}) = E(c\bar{a})$  for any nonzero constant  $c$ , and therefore  $E(\bar{a})$  is finite as long as  $\bar{a} \neq 0$ , since  $N$  is positive definite. Therefore, if there exists a smallest (algebraically) value of  $E$ , say  $E_1$ , which is a stationary state of (5.15) or (5.18), then  $E_1$  must be a minimum value of  $E(\bar{a})$ . Any restriction, then, such as (5.24) on the  $a_i$  can only increase the smallest eigenvalue. Thus, the solution to

$$H\bar{a} = EN\bar{a} \quad (5.25)$$

where  $H$  and  $N$  are now  $n \times n$  matrices and  $\bar{a}$  is an  $n$ -vector provide approximate solutions to

$$H\psi = E\psi \quad (5.14)$$

and in addition, an upper or lower bound to the smallest or largest eigenvalue respectively of (5.14) if such exists.

Let us now consider the solution of equation (5.25). Normally one finds numerical solutions to matrix equations of the form

$$A\bar{y} = \lambda\bar{y} \quad (5.26)$$

where  $A$  is a matrix,  $\bar{y}$  a vector and  $\lambda$  a scalar. There are a variety of ways in which (5.25) may be reduced to this form. We note first that if the set of basis functions  $(f_i)$  were orthonormal, then  $N$  would be equal to  $I$ , and (5.25) would already be in the form (5.26). If this is not the case, one obvious method would be to find the inverse of the matrix  $N$ , and then look for the solutions of



$$N^{-1}H\bar{a} = E\bar{a}. \quad (5.27)$$

This procedure, however, should not be used since it involves considerably more labour than the well known method described below.

Since  $N$  is positive definite it is always possible to write

$$N = MM^T \quad (5.28)$$

where  $M$  is uniquely defined by this equation if we insist that  $M$  be lower triangular, that is,  $M$  have only zeroes above the principal diagonal.  $M$  is relatively easy to find numerically, and equation (5.25) becomes

$$H\bar{a} = EMM^T\bar{a}, \quad (5.29)$$

or multiplying on the left by  $M^{-1}$

$$M^{-1}H\bar{a} = EM^T\bar{a}. \quad (5.30)$$

Let us now define the vector

$$\bar{c} = M^T\bar{a}, \quad (5.31)$$

in which case

$$\bar{a} = (M^{-1})^T\bar{c}, \quad (5.32)$$

and (5.30) now becomes





$$\left[ M^{-1} H (M^{-1})^T \right] \bar{c} = E \bar{c} \quad (5.33)$$

which is in the required form. The eigenvalues of (5.25) can now be found from (5.33) and if necessary one can also find  $\bar{c}$  and thus  $\bar{a}$ .

We note here that  $M^{-1}$  is relatively easy to find, since  $M$  is triangular. The method described above is equivalent to using the Schmidt orthogonalization procedure to replace the original set of basis functions by a new orthonormal set. Assuming orthonormality usually results in a simplification of analysis. As a practical procedure, however, it is usually more convenient to use non-orthonormal basis functions, and then resort to (5.33), rather than (5.25) with  $N = I$ .

### Restricted Cellular Basis Functions

The standard cellular methods described in Chapter IV, for solving  $H\psi = E\psi$  where  $H$  contains a periodic potential all have one feature in common; they all require that the potential  $V(\vec{r})$  be approximated by a spherically symmetric potential inside some sphere. The sphere may be an approximation to the entire unit cell, as in the Wigner - Seitz procedure, or it may be a sphere inside the unit cell, as in the "lattice harmonic" method of Slater. It has been demonstrated by Betts (1959) that this approximation can in some cases lead to serious errors; the more the unit cell deviates from a sphere and the fewer the group operations under which the wave function is invariant the more likely is it that the spherical approximation will lead to inaccuracies. The cellular method described below overcomes these difficulties.

Now, given the equation  $H\psi = E\psi$  we are looking primarily for  $E(\vec{k})$  where  $\psi = e^{i\vec{k} \cdot \vec{r}} u_{\vec{k}}(\vec{r})$ . Basically the method



consists of expanding  $\psi$  in terms of a set of basis functions  $f_i(\vec{r})$ , and then using the variational procedure described in the previous section to determine the energy for a particular value of  $\vec{k}$ . Any periodic potential may be used without resorting to a spherically symmetric approximation, and the boundary conditions, as supplied in part by the Bloch form of  $\psi$ , are satisfied exactly on the surface of the Wigner-Seitz cell.

Having decided to look for  $E(\vec{k})$ , one first requires that subgroup  $G(\vec{k})$  of the point group  $G$  of the lattice, the operations of which either leave  $\vec{k}$  invariant or change  $\vec{k}$  into an equivalent reciprocal lattice vector. Since the irreducible representations of  $G(\vec{k})$  determine the transformation properties of  $\psi_{\vec{k}n} = e^{i\vec{k} \cdot \vec{r}} u_{\vec{k}n}$ , these irreducible representations must now be found in order that the possible symmetries of  $\psi_{\vec{k}n}$  may be determined. Here the range of  $n$  is the number of such irreducible representations, and we note that except for special values of  $\vec{k}$  on lines or planes of symmetry in the first Brillouin zone,  $G(\vec{k})$  will be the identity operator only. In this case the number 1 is the only irreducible representation of  $G(\vec{k})$ , and we find only the uninteresting identity

$$\psi_{\vec{k}1}(I\vec{r}) = 1\psi_{\vec{k}1}(\vec{r}); \quad (5.34)$$

that is,  $\psi$  has no special symmetry properties.

Having determined the possible symmetries of  $\psi$  (assuming that  $\vec{k}$  is on a line or plane of symmetry) one must now decide to which of the irreducible representations  $\psi$  is to correspond. In general, the greater the symmetry of  $\psi$ , the smaller the corresponding eigenvalue. Once the irreducible representation has been chosen, the symmetry conditions which  $\psi$  must satisfy may be tabulated.



Given the symmetry conditions of  $\psi$  it is now possible to determine more stringent boundary conditions which  $\psi$  must satisfy than those supplied by the Bloch conditions

$$\psi(\bar{r}_1) = e^{i\bar{k} \cdot \bar{R}} \psi(\bar{r}_2) \quad (5.35)$$

and

$$\frac{\partial \psi(\bar{r}_1)}{\partial n_1} = -e^{i\bar{k} \cdot \bar{R}} \frac{\partial \psi(\bar{r}_2)}{\partial n_2} . \quad (5.36)$$

Here  $\bar{r}_1$  and  $\bar{r}_2$  are corresponding points on opposite faces of the Wigner-Seitz cell; that is

$$\bar{r}_1 = \bar{R} + \bar{r}_2 \quad (5.37)$$

where  $\bar{R}$  is a lattice vector.

For example, if  $\bar{k} = 0$  equations (5.35) and (5.36) become

$$\psi(\bar{r}_1) = \psi(\bar{r}_2) \quad (5.38)$$

and

$$\frac{\partial \psi(\bar{r}_1)}{\partial n_1} = - \frac{\partial \psi(\bar{r}_2)}{\partial n_2} , \quad (5.39)$$

that is,  $\psi$  must be periodic with the period of the lattice, which is exactly the expected result. Now, if the group  $G$  of the space lattice contains for every boundary point  $\bar{r}_1$







an operation  $g_s$  with corresponding rotation matrix  $S$  such that

$$S\bar{r}_1 = \bar{r}_2, \quad (5.40)$$

then

$$g_s \frac{\partial \psi(\bar{r}_1)}{\partial n_1} = \frac{\partial \psi(S\bar{r}_1)}{\partial (Sn_1)} = \frac{\partial \psi(\bar{r}_2)}{\partial n_2}. \quad (5.41)$$

If, in addition we are considering the identity representation of  $G$ , then

$$g_s \frac{\partial \psi(\bar{r}_1)}{\partial n_1} = (1) \frac{\partial \psi(\bar{r}_1)}{\partial n_1}, \quad (5.42)$$

therefore

$$\frac{\partial \psi(\bar{r}_1)}{\partial n_1} = \frac{\partial \psi(\bar{r}_2)}{\partial n_2}. \quad (5.43)$$

Equations (5.39) and (5.43) together imply that

$$\frac{\partial \psi(\bar{r})}{\partial n} = 0 \quad (5.44)$$

for any vector  $\bar{r}$  on a face of the Wigner-Seitz cell.

On the other hand, consider a representation of the group  $G(\bar{k})$  in which

$$g_s = \pm 1 \quad (5.45)$$



for all elements of the group. In this case, for those points  $\bar{r}_1$  and  $\bar{r}_2$  for which  $g_s = +1$ , condition (5.44) applies; for those faces of the unit cell for which  $g_s = -1$  if  $S\bar{r}_1 = \bar{r}_2$  then

$$g_s \psi(\bar{r}) = \psi(S\bar{r}_1) = \psi(\bar{r}_2), \quad (5.46)$$

and

$$g_s \psi(\bar{r}_1) = (-1) \psi(\bar{r}_1), \quad (5.47)$$

that is

$$\psi(\bar{r}_1) = -\psi(\bar{r}_1). \quad (5.48)$$

Using this result together with equation (5.38), we find that on these faces of the Wigner-Seitz cell

$$\psi(\bar{r}) = 0. \quad (5.49)$$

For values of  $\bar{k} \neq 0$ , and for irreducible representations of degree more than unity, more complicated, though less stringent, boundary conditions may apply. In extreme cases, for example if  $G(\bar{k})$  consists only of the identity operator, then the Bloch conditions themselves may be the most stringent boundary conditions available.

Given the symmetry and boundary conditions that  $\psi$  must satisfy, the basis functions  $f_i(\bar{r})$  may now be constructed. In principle the  $f_i(\bar{r})$  may be taken as linear combinations of any complete set of functions, the linear combinations being chosen such that each  $f_i(\bar{r})$  satisfies both the symmetry conditions and the boundary conditions on  $\psi$ ; clearly then,  $\psi$



which is a linear combination of the  $f$ 's, will also satisfy these conditions exactly. In practice one would use either powers of the coordinates, or the eigensolutions of a Hermitian differential operator to ensure completeness of the original set of functions. In Chapters VI and VII we have used only the powers of  $x, y$ , and  $z$ , and trigonometric functions of the appropriate periodicity, that is, the plane wave solutions of the Helmholtz equation.

Construction of the basis functions  $f_i(\vec{r})$  is not an easy task. For polynomials the procedure consists essentially of writing down the general polynomial

$$P_n(x, y, z) = a_{000} + a_{100}x + \dots + a_{ijk}x^i y^j z^k + \dots + a_{oon}z^n \quad (5.50)$$

for a sufficiently large  $n$ ; the application of the symmetry and boundary conditions to  $P_n$  will result in a large number,  $M$ , of linear homogeneous equations in the  $N$  unknowns  $a_{ijk}$ . Since an infinite number of linearly independent polynomials must exist which satisfy a finite number of consistent conditions, we are guaranteed non-trivial solutions.  $N$ , then must eventually increase faster with  $n$  than does the number of linearly independent equations, resulting in more unknowns than equations. It has been found, in fact, for sufficiently symmetric lattices (in particular, plane hexagonal and face centered cubic) that the  $M$  equations will not be linearly independent, and thus solutions can be found before  $N > M$ .

The computational problem is by no means trivial. For example, in looking for a polynomial  $P$  satisfying only the conditions that  $P$  have the same value, and  $\partial P / \partial n$  have the same magnitude with opposite sign at corresponding points





on opposite edges of a plane hexagon, it was found that the only such polynomial of degree four or less was a constant. Setting

$$P = a_{60}x^6 + a_{51}x^5y + \dots + a_{01}y + a_{00} \quad (5.51)$$

resulted in thirty three homogeneous equations in the twenty eight unknowns  $a_{ijk}$ . These equations have three linearly independent solutions which may be chosen to be of degree zero, five, and six respectively. The use of automatic digital computers in such circumstances as these is almost mandatory.

The difficulty involved in finding the basis functions  $f_i(\vec{r})$  is not without its compensations. Firstly the  $f_i(\vec{r})$ , once found, can be used with a variety of potentials and therefore for different materials having the same structure or with different trial potentials for the same material. And secondly it is not unreasonable to assume that since the boundary and symmetry conditions place such stringent restrictions on the  $f_i(\vec{r})$ , that relatively few such basis functions should be needed in the variational procedure to provide a given level of convergence in the energy. That this is actually the situation at least in some special cases is demonstrated in the following chapters.

Let us now consider the use of trigonometric functions of the appropriate periodicity to construct the basis functions  $f_i(\vec{r})$ . The trigonometric functions are solutions to the Helmholtz equation, and therefore the empty lattice problem. According to Chapter II, then, one can find symmetrized linear combinations of the degenerate states which transform according to the various irreducible representations of  $G(\vec{k})$ . But since the boundary conditions which  $\psi$  must satisfy



do not depend on the particular form of  $V(\vec{r})$ , only on its periodicity, then these symmetrized linear combinations of the trigonometric functions must already satisfy the boundary conditions of  $H\psi = E\psi$  with  $V \neq 0$ , as well as the empty lattice problem. With trigonometric functions, then, the determination of the  $f_i(\vec{r})$  is considerably simplified; once the symmetry conditions appropriate to the choice of  $\vec{k}$  and the irreducible representation have been applied, the boundary conditions must automatically be satisfied.

We note here that if  $\vec{k}$  is not chosen on a line or plane of symmetry of the first Brillouin zone, then the method described in this section reduces merely to an application of the variational procedure. In particular, if the  $f_i(\vec{r})$  are constructed from trigonometric functions then the procedure becomes equivalent to the Plane Wave Method.

#### Consistency Determinant Approach

The method described below, which is similar to Hill's procedure for treating the Mathieu Equation (Hill (1886), McLachlan (1947)) is based on a consistency requirement on  $u_{\vec{k}}(\vec{r})$  where

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_{\vec{k}}(\vec{r}). \quad (5.52)$$

We consider

$$[-\nabla^2 + V(\vec{r})]\psi = E\psi \quad (5.53)$$

Where  $V(\vec{r})$  is periodic; if we substitute (5.52) into equation (5.53), we find that  $u_{\vec{k}}(\vec{r})$  must satisfy the equation



$$\nabla^2 u + 2i\bar{k} \cdot \nabla u + (E - \bar{k} \cdot \bar{k} - V)u = 0. \quad (5.54)$$

Let us now separate  $u_{\bar{k}}(\bar{r})$  into its real and imaginary parts, and write

$$u(\bar{r}) = \alpha(\bar{r}) + i\gamma(\bar{r}) ; \quad (5.55)$$

substituting (5.55) into equation (5.54) yields the two real equations

$$\nabla^2 \alpha - 2\bar{k} \cdot \nabla \gamma + (E - \bar{k} \cdot \bar{k} - V)\alpha = 0 \quad (5.56)$$

and

$$\nabla^2 \gamma + 2\bar{k} \cdot \nabla \alpha + (E - \bar{k} \cdot \bar{k} - V)\gamma = 0. \quad (5.57)$$

We now expand both  $\alpha(\bar{r})$  and  $\gamma(\bar{r})$  in terms of a set of basis functions  $f_i(\bar{r})$ :

$$\alpha(\bar{r}) = \sum_j a_j f_j(\bar{r}) \quad (5.58)$$

and

$$\gamma(\bar{r}) = \sum_j c_j f_j(\bar{r}). \quad (5.59)$$





Substituting the expansions for  $\alpha(\vec{r})$  and  $v(\vec{r})$  into equation (5.56) gives

$$\sum_j a_j \nabla^2 f_j - 2 \sum_j c_j \vec{k} \cdot \nabla f_j + (E - \vec{k} \cdot \vec{k}) \sum_j a_j f_j - \sum_j a_j V f_j = 0. \quad (5.60)$$

Let us now define the matrices  $L, N, A(\vec{k})$ , and  $V$  by the following equations

$$L_{ij} = \int f_i(\vec{r}) \nabla^2 f_j(\vec{r}) d\tau \quad (5.61)$$

$$A_{ij}(\vec{k}) = \int f_i(\vec{r}) \vec{k} \cdot \nabla f_j(\vec{r}) d\tau \quad (5.62)$$

$$N_{ij} = \int f_i(\vec{r}) f_j(\vec{r}) d\tau \quad (5.63)$$

$$V_{ij} = \int f_i(\vec{r}) V(\vec{r}) f_j(\vec{r}) d\tau \quad (5.64)$$

where each of the integrations is over the Wigner-Seitz cell. If we now multiply equation (5.60) by  $f_i(\vec{r})$  and integrate over the unit cell we find, using the definitions (5.61) to (5.64), the  $i$ 'th row of the matrix equation

$$(L + (E - \vec{k} \cdot \vec{k})N - V)\vec{a} - 2A(\vec{k})\vec{c} = \vec{0}, \quad (5.65)$$

where the coefficients  $a_i$  and  $c_i$  comprise the vectors  $\vec{a}$  and  $\vec{c}$  respectively. Since we could have multiplied (5.60) by any of the basis functions  $f_i(\vec{r})$ , it is clear that the entire matrix equation holds.

Similarly, if we substitute the expansion (5.58) and (5.59) into equation (5.57), and then multiply by  $f_i(\vec{r})$  and integrate, it is easy to show that



$$(L+(E-\bar{k}\cdot\bar{k})N-V)\bar{c}+2A(\bar{k})\bar{a} = 0. \quad (5.66)$$

Clearly, then if we want non-trivial solutions for the vectors  $\bar{a}$  and  $\bar{c}$ , then equations (5.65) and (5.66) imply that the determinant of the matrix  $C(E,\bar{k})$  must vanish, where

$$C(E,\bar{k}) = \begin{pmatrix} L+(E-\bar{k}\cdot\bar{k})N-V & -2A(\bar{k}) \\ +2A(\bar{k}) & L+(E-\bar{k}\cdot k)N-V \end{pmatrix} \quad (5.67)$$

If we use  $M$  basis functions  $f_i(\bar{r})$ , then  $C(E,\bar{k}) = 0$  provides an approximate  $(\bar{E},\bar{k})$  relationship, where  $C$  is a  $(2M)\times(2M)$  matrix.

The labour involved in evaluating determinants of large order is not insignificant, and therefore the  $M\times M$  formulation derived below is considerably more convenient.

Let  $A$  and  $B$  be arbitrary  $M\times M$  matrices: we consider now the problem of reducing the  $2M\times 2M$  matrix

$$\begin{pmatrix} A & -B \\ B & A \end{pmatrix} \quad (5.68)$$

to the block diagonal form

$$\begin{pmatrix} C & 0 \\ 0 & D \end{pmatrix} \quad (5.69)$$

where  $C$  and  $D$  are also  $M\times M$ . We treat the problem much as if



A and B were scalars.

Let a and b be scalar multiples of the  $M \times M$  unit matrix I, and assume that L is an  $M \times M$  matrix such that

$$\begin{pmatrix} A & -B \\ B & A \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} a \\ b \end{pmatrix} L. \quad (5.70)$$

The matrix equation (5.70) may be rewritten as the pair of matrix equations

$$(A-L)a - Bb = 0 \quad (5.71)$$

$$Ba + (A-L)b = 0. \quad (5.72)$$

Solving both (5.71) and (5.72) for  $(A-L)$  we find respectively

$$A-L = Bba^{-1} \quad (5.73)$$

and

$$A-L = -Bab^{-1}; \quad (5.74)$$

therefore

$$ba^{-1} = -ab^{-1}. \quad (5.75)$$

Let

$$ba^{-1} = c, \quad (5.76)$$





where the matrix  $c$  is also a scalar multiple of the  $M \times M$  unit matrix  $I$ , since both  $a$  and  $b$  are. From (5.76)

$$ab^{-1} = c^{-1}, \quad (5.77)$$

but from (5.75) and (5.76)

$$ab^{-1} = -ba^{-1} = -c, \quad (5.78)$$

therefore

$$c^{-1} = -c, \quad (5.79)$$

and so

$$c^2 = -I. \quad (5.80)$$

And since  $c$  is a multiple of  $I$  it follows then that

$$c_{jj} = \pm i, \quad j = 1, 2, \dots, M. \quad (5.81)$$

Let us set

$$a = I, \quad (5.82)$$

and

$$b = \mp iI, \quad (5.83)$$

$$c = \pm iI, \quad (5.84)$$



where we use either the top or the bottom row of signs.  
Equation (5.70), together with equations (5.82) to (5.84)  
now yields

$$\begin{aligned}
 \begin{pmatrix} A & -B \\ B & A \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} &= \begin{pmatrix} A & -B \\ B & A \end{pmatrix} \begin{pmatrix} I \\ \mp iI \end{pmatrix} \\
 &= \begin{pmatrix} A \pm iB \\ B \mp iA \end{pmatrix} \\
 &= \begin{pmatrix} I \\ \mp iI \end{pmatrix} (A \pm iB). \quad (5.85)
 \end{aligned}$$

Therefore

$$\begin{pmatrix} A & -B \\ B & A \end{pmatrix} \begin{pmatrix} I & I \\ -iI & iI \end{pmatrix} = \begin{pmatrix} I & I \\ -iI & iI \end{pmatrix} \begin{pmatrix} A+iB & 0 \\ 0 & A-iB \end{pmatrix}; \quad (5.86)$$

and since

$$\begin{pmatrix} I & I \\ -iI & iI \end{pmatrix}^{-1} = \frac{1}{2} \begin{pmatrix} I & iI \\ I & -iI \end{pmatrix} \quad (5.87)$$



we find that

$$(1/2) \begin{pmatrix} I & iI \\ I & -iI \end{pmatrix} \begin{pmatrix} A & -B \\ B & A \end{pmatrix} \begin{pmatrix} I & I \\ -iI & iI \end{pmatrix} = \begin{pmatrix} A+iB & 0 \\ 0 & A-iB \end{pmatrix} \quad (5.88)$$

Therefore

$$\begin{aligned} \Delta &= \begin{vmatrix} A & -B \\ B & A \end{vmatrix} = \begin{vmatrix} A+iB & 0 \\ 0 & A-iB \end{vmatrix} \\ &= |A+iB| |A-iB| \quad (5.89) \end{aligned}$$

And since

$$(A-iB) = (A+iB)^* \quad (5.90)$$

implies that

$$|A-iB| = |A+iB|^* \quad (5.91)$$

where \* means complex conjugate, then

$$\Delta = |\det(A+iB)|^2. \quad (5.92)$$

We find, then, that setting

$$|c(E, \vec{k})| = C \quad (5.93)$$





where  $C(E, \bar{k})$  is given by equation (5.67), is equivalent to setting

$$|D(E, \bar{k})| = 0 \quad (5.94)$$

where

$$D(E, \bar{k}) = L + (E - \bar{k} \cdot \bar{k})N - V + 2iA(\bar{k}). \quad (5.95)$$

Since, according to Bloch's Theorem,  $u_{\bar{k}}(\bar{r})$  is periodic with the period of the lattice, then the  $f_i(\bar{r})$  used to expand the real and imaginary parts of  $u$  must be periodic or at least satisfy periodic boundary conditions on the surface of the Wigner-Seitz cell. In this case it is clear that the matrices  $L, N$  and  $V$  are symmetric and the matrix  $A(\bar{k})$  antisymmetric, and therefore  $D(E, \bar{k})$  is Hermitian. Given that  $D(E, \bar{k})$  is Hermitian, there exists a matrix  $S$  such that  $S^{-1}D(E, \bar{k})S$  is both diagonal and real, and since

$$|S^{-1}D(E, \bar{k})S| = |S^{-1}| |D(E, \bar{k})| |S| = |D(E, \bar{k})| \quad (5.96)$$

for any  $E$  and  $\bar{k}$ , it is clear that the values of  $E$ , given  $\bar{k}$ , which satisfy (5.94) are, as expected, real. Furthermore, in the special cases treated in the following chapters it has been found that the elements of  $D(E, \bar{k})$  are not complex, but are either real or imaginary in such a fashion as to permit the multiplication of alternate rows and columns by  $i$  to obtain a determinant consisting entirely of real elements. This greatly facilitates the evaluation of specific points  $(E, \bar{k})$  from the implicit approximate dispersion relation  $|D(E, \bar{k})| = 0$ .



### Interpolation Procedure

The methods described in the two proceeding sections may be combined in the manner outlined below.

The method of restricted cellular basis functions should provide, once the potential and the basis functions themselves are available, accurate values of  $E(\bar{k})$  for only a modest outlay of labour. One must evaluate the integrals

$$L_{ij} = \int f_i \nabla^2 f_j d\tau \quad (5.97)$$

$$V_{ij} = \int f_i V f_j d\tau \quad (5.98)$$

and

$$N_{ij} = \int f_i f_j d\tau, \quad (5.99)$$

and then the lower eigenvalues of the matrix equation

$$H\psi = (-L+V)\psi = EN\psi \quad (5.100)$$

must be found. Standard library programs are usually available to solve equation (5.100) on a digital computer, as are integration routines requiring only the writing of an integrand subroutine, for the evaluation of the matrices  $L$ ,  $V$ , and  $N$ . On the other hand the initial determination of the basis functions  $f_i$  is not simple, and also the method can only be expected to be convenient for those values of  $\bar{k}$  on lines or planes of symmetry in the first Brillouin zone; the more symmetric the point  $\bar{k}$ , the more severe the restrictions on the basis functions  $f_i$ , and therefore the fewer the number of basis functions required in the variational procedure.



The determinantal method described in the preceeding section, on the other hand, provides one with an approximation to the entire dispersion relation. In this case, the basis functions being much less stringently restricted are much easier to find. But for exactly this reason one would expect to require a correspondingly larger matrix to provide a given level of convergence.

It seems natural, then, to follow the example of Slater and Koster (1954) and combine the methods described in the two proceeding sections. The consistency determinant provides an implicit dispersion relation involving, besides  $E$  and  $\bar{k}$ , the quantities

$$\int f_i Q f_j d\tau, \quad (5.101)$$

where  $Q$  is any one of  $1, \nabla^2, V$ , or  $\nabla$ . These latter quantities may be treated as parametrs; they may be evaluated exactly, or by using a least squares technique, to ensure that the interpolative dispersion relation fits at the symmetry points  $(E, \bar{k})$  determined by the method of restricted cellular basis functions.





## CHAPTER VI

APPLICATION OF NEW METHODS

In this chapter the three new methods developed in Chapter V are applied to various models. The applications are intended to illustrate both the use of the methods and the rates of convergence in some special cases.

The Empty Lattice

The  $(E,k)$  relationship, as  $V(x)$  approaches zero, becomes

$$E = (k - n\pi)^2, \quad n = 0, \pm 1, \pm 2, \dots \quad (6.1)$$

where  $V(x+2n) = V(x)$ . In this section the approximations to (6.1) are found by using the consistency determinant with various types of basis functions.

If we use as basis functions

$$\begin{aligned} f_1 &= 1/\sqrt{2} \\ f_{2n} &= \sin n\pi x \\ f_{2n+1} &= \cos n\pi x, \quad n > 1 \end{aligned} \quad (6.2)$$

then the following results are easily obtained

$$L_{ij} = 0, \quad i \neq j$$

$$L_{11} = 0$$



$$L_{mm} = \begin{cases} -(m\pi/2)^2, & m \text{ even} \\ -[(m-1)\pi/2]^2, & m \text{ odd.} \end{cases} \quad (6.3)$$

$$N_{nm} = \delta_{nm}. \quad (6.4)$$

$$\xi_{2m,2m+1} = -m\pi$$

$$\xi_{2m+1,2m} = m\pi \quad (6.5)$$

$$V_{nm} = 0. \quad (6.6)$$

Here  $\xi_{ij} = \int f_i (df_j/dx) dx$ .

Using only the first basis function, the matrix  $[L + N(E-k^2) - V + 2ik\xi]$  becomes  $(E-k^2)$  and we find exactly the lowest branch of the dispersion relation in the first Brillouin zone,  $-\pi/2 < k < \pi/2$ .

Using the first two functions, we find

$$(E-k^2)(E-k^2-\pi^2) = 0; \quad (6.7)$$

that is  $E = k^2$  which is the correct lowest branch of the dispersion relation, and  $E = k^2 + \pi^2$  which bears no relation to the correct relation.

If we use the first three basis functions, we find

$$(E-k^2)(E-(k-\pi)^2)(E-(k+\pi)^2) = 0; \quad (6.8)$$

that is, the lowest three branches of the  $(E,k)$  relation in the first Brillouin zone are obtained exactly.



In general, the consistency determinant consists of  $(E-k^2)$  in the (1,1) position, followed by  $n$   $2 \times 2$  blocks along the main diagonal, each of the form

$$\begin{pmatrix} E-k^2-m^2\pi^2 & -2m\pi ik \\ 2m\pi ik & E-k^2-m^2\pi^2 \end{pmatrix}, \quad m=1,2,\dots,n$$

where the first  $(2n+1)$  functions are used; and if the  $(2n+2)$ 'th function is used also, the last  $2 \times 2$  block is followed by  $E-k^2-(n+1)\pi^2$  in the  $(2n+2,2n+2)$  position.

Clearly, then, using the first  $2n+1$  basis functions provides exactly the first  $2n+1$  curves in the first Brillouin zone, and including the  $(2n+2)$ 'th basis function given only an extraneous root. That exact answers are obtained is not surprising; the basis functions used are the eigensolutions to the problem. That the basis functions need be added in pairs is not obvious, and seems to be related to the symmetry of  $E(k)$ , that is, the symmetry of  $V(x)$ .

Let us now consider the use of polynomial basis functions with the consistency determinant. If we choose

$$f_{i+1} = x^i, \quad i = 0,1,2,\dots \quad (6.9)$$

then setting the determinant equal to zero yields

$$(E-k^2)^n = 0 \quad (6.10)$$

when  $n$  basis functions are used. The difficulty, of course, is that the  $f$ 's do not satisfy the periodic boundary conditions which  $u(x)$  must satisfy. If the more sensible basis functions





$$\begin{aligned}
f_1 &= 1 \\
f_2 &= x^3 - x \\
f_3 &= x^4 - 2x^2
\end{aligned} \tag{6.11}$$

which satisfy the boundary conditions

$$\begin{aligned}
f_i(-1) &= f_i(1) \\
f_i'(-1) &= f_i'(1)
\end{aligned} \tag{6.12}$$

are used then the following results are easily obtained.  
 $L+N(E-k^2)-V+2ik\xi$  becomes

$$\begin{array}{ccc}
2(E-k^2) & 0 & -\frac{14}{15}(E-k^2) \\
0 & -\frac{8}{5} + \frac{16}{105}(E-k^2) & \frac{128}{105} ki \\
-\frac{14}{15}(E-k^2) & -\frac{128}{105} ki & -\frac{256}{105} + \frac{214}{315}(E-k^2)
\end{array} \tag{6.13}$$

Expression (6.13), using only one basis function yields  $E = k^2$  as expected. Using two basis functions we find, besides  $E = k^2$ ,

$$E = 21/2 + k^2. \tag{6.14}$$

This is not an improvement, and would seem to correspond to the extraneous curve  $E = k^2 + \pi^2$  for the trigonometric basis



functions when  $n = 2$ . For  $n = 3$ , (6.13) yields  $E = k^2$  and

$$2(E-k^2)^2 - 41(E-k^2) + 210 - 80k^2 = 0 \quad (6.15)$$

which gives

$$E = k^2 + 10.25 \pm .25(1 + 640k^2)^{1/2}. \quad (6.16)$$

Figure 4, may be used to illustrate the situation. Using the minus sign gives the middle solid curve ( $-\pi/2 \leq k \leq \pi/2$ ), and the plus sign gives the upper solid curve. These two curves form approximations to the parabolic segments  $E = (k-\pi)^2$  and  $E = (k+\pi)^2$ ,  $-\pi/2 \leq k \leq \pi/2$ . The following table illustrates the accuracy of the approximation.

Table I

K	E-	E <sub>-exact</sub>	E+	E <sub>+exact</sub>
0.0	10.00	9.87	10.50	9.37
0.1	9.60	9.25	10.94	10.51
0.2	9.00	8.65	11.58	11.17
0.5	7.33	6.98	13.67	13.26
1.0	4.92	4.59	17.58	17.15
1.5	3.01	2.69	21.99	21.54
$\pi/2$	2.78	2.47	22.65	22.21

The polynomial basis functions "find it difficult" to approximate



the intersecting of the two parabolas  $E = (k \pm \pi)^2$ , akin to the well known difficulty in finding a polynomial approximation for  $|x|$ , and is not likely to cause trouble in a lattice with  $V \neq 0$ .

### The Kronig-Penny Model

We now consider the solution to

$$(-\nabla^2 + V)\psi = E\psi \quad (6.17)$$

where

$$V(x) = 2V\delta(x-2n). \quad (6.18)$$

The exact dispersion relation for the problem is easily found to be

$$\cos 2k = \cos 2\sqrt{E} + 2V \frac{\sin 2\sqrt{E}}{2\sqrt{E}} \quad (6.19)$$

(see, for example, Jones (1960)).

Let us consider first the method of restricted basis functions. For the Kronig-Penny problem the point group  $G$  of the lattice consists only of two elements  $G_1$  and  $G_2$  where  $G_1 x = x$  and  $G_2 x = -x$ . The two irreducible representations of the group are the identity representation and the alternating representation. Both representations apply to the only two points of symmetry  $k = 0$  and  $k = \pi$ , and so we have in total, four cases. The boundary conditions which the basis functions must satisfy are easily found, and are as follows:





Identity representation,  $k = 0$

$$p(-x) = p(x)$$

$$p'(\pm 1) = 0 \quad (6.20)$$

Alternating representation,  $k = 0$

$$q(-x) = -q(x)$$

$$q(\pm 1) = 0 \quad (6.21)$$

Identity representation,  $k = \pi/2$

$$r(-x) = r(x)$$

$$r(\pm 1) = 0 \quad (6.22)$$

Alternating representation,  $k = \pi/2$

$$s(-x) = -s(x)$$

$$s'(\pm 1) = 0. \quad (6.23)$$

The basis functions for the four cases are easily found:

$$p_n(x) = nx^{2n-2} - (n-1)x^{2n} \quad (6.24)$$

$$q_n(x) = x^{2n-1} - x^{2n-3} \quad (6.25)$$

$$r_n(x) = x^{2n-2} - x^{2n-4} \quad (6.26)$$

$$\text{and } s_n(x) = (2n+1)x^{2n-1} - (2n-1)x^{2n+1}. \quad (6.27)$$

Let us consider the alternating representation for  $k = 0$ ;



the other cases are treated in an almost identical fashion. We need first the matrices

$$L_{ij} = \int_{-1}^1 q_i(x) q_j''(x) dx \quad (6.28) \quad (6.28)$$

$$V_{ij} = \int_{-1}^1 q_i(x) V(x) q_j(x) dx \quad (6.29)$$

$$N_{ij} = \int_{-1}^1 q_i(x) q_j(x) dx. \quad (6.30)$$

The matrix  $V$  is identically zero, since  $q_j(0) \equiv 0$ , and  $L$  and  $N$  are easily evaluated exactly;  $L$  and  $N$  are symmetric, and typical elements are  $L_{11} = -24/15$ , and  $N_{11} = 16/105$ . Using successively the first 1,2,3 and 4 basis functions we find the eigenvalues of  $H\bar{a} = EN\bar{a}$  where  $H = -L+V = -L$ . The following table results

Table II

n	$E_1$	$E_2$
1	10.50000	-----
2	9.87539	50.12461
3	9.86962	39.99799
4	9.86961	39.48929
...	...	...
$\infty$ (exact)	9.86960	39.47842



That  $V$  is identically zero is not surprising; equation (6.19) implies that every second root  $E$  for  $k = 0$  is given by

$$2\sqrt{E} = 2n\pi \quad (6.13)$$

or

$$E = (n\pi)^2 \quad (6.32)$$

Then  $E_1 = \pi^2$  and  $E_2 = 4\pi^2$ , regardless of the strength of the delta function potential. The convergence is quite rapid, and the alternate roots (which do depend on  $V$ ) for  $k = 0$ , and the roots for  $k = \pi/2$  are easily found in the same manner. Again, Figure 4 is a good illustration of the situation.

Let us now apply the consistency determinant to the Kronig-Penny model, with  $V = 1/2$ , i.e.  $V(x) = \sum \delta(x-2n)$ . We consider first the trigonometric basis functions

$$f_1 = 1/\sqrt{2}$$

$$f_{2n} = \sin n\pi x$$

$$f_{2n+1} = \cos n\pi x, \quad n > 1. \quad (6.2)$$

The matrices  $L$ ,  $N$  and  $\xi$  have already been used for the empty lattice and are given by equations (6.3) to (6.5) inclusive, only the matrix  $V$  is now required.  $V$  is given by

$$V_{ij} = f_i(0) f_j(0), \quad (6.33)$$





and so

$$V_{11} = 1/2$$

$$V_{1,2j} = V_{2j,1} = 1/\sqrt{2}$$

$$V_{2j,2j} = 1$$

$$V_{ij} = 0 \text{ otherwise.} \quad (6.34)$$

For  $n = 1$  we find

$$E = 1/2 + k^2. \quad (6.35)$$

For  $n = 2$  equation (6.35) holds, and we also find the extraneous curve

$$E = \pi^2 + k^2. \quad (6.36)$$

With the first three basis functions we find

$$2(E-k^2-1/2)[(E-k^2-\pi^2)(E-k^2-\pi^2-1)-4k^2\pi^2] - (E-k^2-\pi^2) = 0. \quad (6.37)$$

At  $k = 0$  the three roots of (6.37) are .45200,  $\pi^2$ , and 10.91760, whereas the correct values are .42695,  $\pi^2$  and 10.84276. At  $k = \pi/2$  the three roots are  $\pi^2/4 = 2.46740$ , 3.44145, and 22.73256, while the corresponding exact solutions are  $\pi^2/4 = 2.46740$ , 3.37374 and 22.20657. The solutions to (6.37) are found in tables IV, V, and VI.

Let us now use the consistency determinant with polynomial basis functions satisfying the periodic boundary conditions (6.12). One such set of basis functions is



$$\begin{aligned}
f_1 &= 1 \\
f_{2n} &= x^{2n+1} - x^{2n-1} \\
f_{2n+1} &= x^{2n+2} - \frac{n}{n+1} x^{2n}, \quad n \geq 1.
\end{aligned} \tag{6.38}$$

The matrices  $L$ ,  $N$ ,  $V$  and  $\xi$  are found to be:

$$\begin{aligned}
L_{n1} &= L_{1n} = 0 \\
L_{2n+1,2m} &= L_{2n,2m+1} = 0 \\
L_{2n,2m} &= \frac{-8(8mn-2m-2n-1)}{(2m+2n+1)(2m+2n-1)(2m+2n-3)} \\
L_{2n+1,2m+1} &= \frac{-64(m+1)(n+1)}{(2m+2n+3)(2m+2n+1)(2m+2n-1)} \tag{6.39} \\
N_{11} &= 2 \\
N_{1,2n} &= 0 \\
N_{1,2n+1} &= \frac{-2(4n+3)}{n(2n+1)(2n+3)} \\
N_{2n,2m+1} &= N_{2n+1,2m} = 0 \\
N_{2n,2m} &= \frac{16}{(2n+2m+3)(2n+2m+1)(2n+2m-1)} \\
N_{2n+1,2m+1} &\equiv \frac{2(8m^2+24mn+8n^2+26m+26n+15)}{mn(2m+2n+5)(2m+2n+3)(2m+2n+1)} \tag{6.40}
\end{aligned}$$



$$\xi_{i1} = \xi_{1i} = 0$$

$$\xi_{2n+1,2m} = -\xi_{2n,2m+1} = \frac{-32(n+1)}{(2m+2n+3)(2m+2n+1)(2m+2n-1)}$$

$$\xi_{ij} = 0 \text{ otherwise} \quad (6.41)$$

and

$$V_{ij} = 0 \text{ if } ij \neq 1$$

$$V_{11} = 1 \quad (6.42)$$

Using only the first polynomial basis function, we find, as we did for the trigonometric basis,

$$E = 1/2 + k^2, \quad (6.43)$$

and using the first two basis functions gives, as well as (6.43), the extraneous root

$$E = 21/2 + k^2 \quad (6.44)$$

which corresponds to (6.36) for the trigonometric approximation to the Kronig-Penny model, and to the extraneous curves when  $n = 2$  for the empty lattice. If the first three basis functions are used, one obtains

$$\begin{aligned} &5(E-k^2-1/2)(2(E-k^2)-21)(107(E-k^2)-384) \\ &-343(E-k^2)^2(2(E-k^2)-21)-15360k^2(E-k^2-1/2) = 0. \end{aligned} \quad (6.45)$$





At  $k = 0$  the three roots are .45720, 10.5, and 10.93605 as opposed to the exact solutions .42695,  $\pi^2 = 9.86960$  and 10.84276; at  $k = \pi/2$  the roots of (6.45) are 2.60478, 3.57879 and 23.11187, while the true roots are 2.46740, 3.37374 and 22.20657. The solutions to (6.45) appear in tables IV, V and VI.

Using the first four basis functions produces only an insignificant improvement in the three lowest  $(E, k)$  curves; the results for  $n = 4$  agree with those for  $n = 3$  to almost three figures. This corresponds to the empty lattice situation in which the symmetry of the problem appears to demand that the basis functions be added in pairs to improve the approximation. We would expect, then to get an improvement for  $n = 5$ , and this is indeed the case, as illustrated in the following table.

Table III

$n$	$E_1(0)$	$E_2(0)$	$E_3(0)$
1	.5	-	-
3	.45720	10.5	10.93605
5	.44625	9.87539	10.89079
...	...	...	...
$\infty$	.42695	9.86960	10.84276

The error in the smallest root at  $n = 5$  is less than  $2/3$  of the error in the corresponding root at  $n = 3$ .



Let us now use the consistency determinant as an interpolation aid. We will use exact values for  $E$  at the symmetry points  $k = 0$  and  $\pi/2$ , though normally these values would be determined by using restricted basis functions. If we assume a one basis function form, then we have

$$a + b(E - k^2) + ick = 0 \quad (6.46)$$

where  $a = L - V$ ,  $b = N$  and  $C = 2\xi$  are to be determined by insisting that the solution  $E(k)$  to (6.46) pass through given points. Since  $E$  must be real,  $c = 0$ , and it was found in general that dropping the Hermiticity requirement on the matrix never helps. If we now fit at the point  $E = .42695$ ,  $k = 0$  we find

$$E = .42695 + k^2. \quad (6.47)$$

Equation (6.47) evaluated at  $K = \pi/2$  gives  $E = 3.89435$  instead of 2.41740.

Assuming a two basis function form allows us to fit at the points

$$E(0) = .42695$$

$$E(\pi/2) = 2.46740$$

$$E(\pi/2) = 3.37374. \quad (6.48)$$

The resulting dispersion relation is

$$E^2 - (2k^2 + .90634)E + (k^4 + .82339k^2 + .20467) = 0, \quad (6.49)$$



which gives, besides the values (6.48) the root

$$E(0) = .4813. \quad (6.50)$$

That is, a pair of "nested" curves similar to the result for  $n = 2$  in the previous cases.

If we now assume a three basis function form, we find that the dispersion relation can be made to fit at five points; the points used were those in (6.48), and

$$E(0) = 9.86960$$

$$E(0) = 10.84276. \quad (6.51)$$

The resulting dispersion relation is

$$E^3 - (3k^2 + 21.14315)E^2 + (3k^4 + 2.32846k^2 + 115.89971)E - (k^6 - 18.81468k^4 + 96.99219k^2 + 45.70704) = 0. \quad (6.52)$$

The interpolation procedure works well between the given points and also as an extrapolation aid in the third curve, for example the third root of (6.52) is  $E(\pi/2) = 22.60420$  as opposed to 22.20656; the error here is less than 1.8%. The symmetry of the problem again seems to demand an odd number of basis functions.

The various approximations to the three lowest curves of  $E(\bar{k})$  are tabulated below;  $E_a$  is the analytic solution,  $E_p$  is the approximation using three polynomial basis functions,  $E_t$  uses three trigonometric basis functions, and  $E_d$  is the solution obtained from the consistency determinant fitted at





$k = 0$  and  $k = \pi/2$  on the two lowest curves, and  $k = 0$  only on the third curve.

Table IV

$k$	$E_a$	$E_p$	$E_t$	$E_d$
0.0	.42695	.45720	.45200	.42695
0.1	.43658	.46704	.46181	.43680
0.2	.46602	.49654	.49122	.46619
0.5	.67173	.70272	.69667	.67173
1.0	1.39745	1.43118	1.42027	1.39567
1.5	2.42002	2.50825	2.42405	2.38691
$\pi/2$	2.46740	2.60478	2.46740	2.46740

Table V

$k$	$E_a$	$E_p$	$E_t$	$E_d$
0.0	9.86960	10.50000	9.86960	9.86960
0.1	9.57226	10.06036	9.58673	9.56621
0.2	9.05106	9.47739	9.07534	9.04717
0.5	7.43660	7.80774	7.46962	7.42121
1.0	5.08976	5.42391	5.12960	5.05355
1.5	3.42953	3.68792	3.49389	3.41519
$\pi/2$	3.37374	3.57879	3.44148	3.37374





Table VI

k	E <sub>a</sub>	E <sub>p</sub>	E <sub>t</sub>	E <sub>d</sub>
0.0	10.84276	10.93605	10.91760	10.84276
0.1	11.15673	11.39584	11.22067	11.17014
0.2	11.73819	12.03927	11.79265	11.74979
0.5	13.77463	14.13278	13.82293	13.80022
1.0	17.63365	18.03817	17.68934	17.68894
1.5	21.87569	22.44708	22.07127	22.09105
$\pi/2$	22.20657	23.11187	22.73256	22.60420

#### The Plane Hexagonal Lattice

In this section we consider briefly the application of the new methods to a plane hexagonal lattice with two different potentials. The Wigner-Seitz cell and the Brillouin zone for this lattice are illustrated in Figures 1 and 2 respectively. Trigonometric basis functions for the consistency determinant are easy to find, since the general functions

$$\sin 2\pi \left( \frac{2n-m}{\sqrt{3}} x + my \right)$$

$$\cos 2\pi \left( \frac{2n-m}{\sqrt{3}} x + my \right) \quad n, m = 0, \pm 1, \pm 2, \dots \quad (6.53)$$

have the appropriate periodicity. The second derivative of each of the expressions in (6.53) is  $(-16\pi^2/3)g(m,n)$  times itself, where

$$g(m,n) = m^2 - mn + n^2 \quad (6.54)$$



We choose the basis functions to be of the form (6.53), and partially order them in the order of increasing  $g$ . If we choose  $(m,n)$  to be  $(0,0)$ ,  $(0,1)$ ,  $(1,0)$ ,  $(1,1)$ ,  $(1,2)$ ,  $(-1,1)$ ,  $(2,1)$ ,  $(0,2)$ ,  $(2,2)$  and  $(2,0)$  then  $g$  is  $0,1,1,1,3,3,3,4,4$  and  $4$  respectively, and there are no other choices of  $m$  and  $n$  which give  $g \leq 4$ . The first few basis functions are chosen to be

$$\begin{aligned} f_1 &= 1/\sqrt{2} \\ f_2 &= \sin 2\pi \left( \frac{2x}{\sqrt{3}} \right) \\ f_3 &= \cos 2\pi \left( \frac{2x}{\sqrt{3}} \right) \\ f_4 &= \sin 2\pi \left( \frac{x}{\sqrt{3}} + y \right), \end{aligned} \tag{6.55}$$

and the basis functions form an orthogonal set such that

$$\int f_i^2 d\tau = \sqrt{3}/4. \tag{6.56}$$

The matrix  $N$ , then, is  $(\sqrt{3}/4)I$ . The matrix  $L$  is diagonal, with

$$\begin{aligned} L_{11} &= 0 \\ L_{ii} &= -(4\pi^2/\sqrt{3})g_i \\ g_i &= 1 \quad i=2,3,\dots,7 \\ &= 3 \quad i=8,9,\dots,13. \end{aligned} \tag{6.57}$$



The matrices

$$\xi_{ij} = \int f_i \frac{\partial f_j}{\partial x} d\tau \quad (6.58)$$

$$\eta_{ij} = \int f_i \frac{\partial f_j}{\partial y} d\tau \quad (6.59)$$

are zero except for elements like (2,3), (3,2), (4,5), (5,4), (6,7), (7,6), etc. The first few elements are

$$\begin{aligned} \xi_{23} &= - \xi_{32} = - \pi \\ \xi_{45} &= - \xi_{54} = - \pi/2 \\ \xi_{67} &= - \xi_{76} = - \pi/2 \end{aligned} \quad (6.60)$$

and

$$\begin{aligned} \eta_{23} &= - \eta_{32} = 0 \\ \eta_{45} &= - \eta_{54} = - \pi\sqrt{3}/2 \\ \eta_{67} &= - \eta_{76} = + \pi\sqrt{3}/2 \end{aligned} \quad (6.61)$$

The potential  $V(x,y)$  was chosen to be a two dimensional analogue of the Kronig-Penny potential.  $V$  is zero inside every Wigner-Seitz cell, and infinite on the boundary of the cells in such a fashion that the integral of  $V$  over any area is the length of the boundary included in the area. The





matrix  $V$ , then, is given by

$$V_{ij} = \int f_i V f_j d\tau = 1/2 \oint f_i f_j ds \quad (6.62)$$

where  $s$  is the edge of the Wigner-Seitz cell in Figure 1. The matrix  $V$  is clearly symmetric, and the first few elements are

$$\begin{aligned} V_{11} &= \sqrt{3}/2 \\ V_{12} &= 0 \\ V_{22} &= \frac{\sqrt{3}}{2} - \frac{9}{16\pi} . \end{aligned} \quad (6.63)$$

The consistency determinant was set up for  $n = 1, 2, 3, \dots, 7$ , and the successive values of the lowest energy for  $\bar{k} = \bar{0}$  are

TABLE VII

$n$	$E(0)$
1	2.00000
2	2.00000
3	1.97423
4	1.97423
5	1.94833
6	1.94833
7	1.92229

One expects the eigenfunction corresponding to the lowest eigenvalue for  $\bar{k} = \bar{0}$  to be even, and since  $f_2$ ,  $f_4$  and  $f_6$  are sines, it is not surprising that they produce no improvement



in  $E_1$ . For  $n = 7$  the remaining six values of  $E$  vary between

$$52.7 \leq E \leq 57.2 \quad (6.64)$$

and represent very poor approximations to the second and third values of  $E(0)$ .

Let us now use polynomial basis functions satisfying periodic boundary conditions. The first three such polynomials may be chosen as

$$\begin{aligned} f_1 &= 1 \\ f_2 &= 20x^2y^3 + 4y^5 - 5x^2y - 5y^3 + y \\ f_3 &= 12x^6 + 60x^2y^4 + 8y^6 - 15x^4 \\ &\quad - 30x^2y^2 - 15y^4 + 6x^2 + 6y^2 \end{aligned} \quad (6.65)$$

We note here that  $f_3$  is by chance invariant under all of the group operations which leave the hexagon invariant, and also that  $\partial f / \partial n = 0$  on the boundary of the hexagon.  $f_3$ , then, is a "restricted" polynomial for the identity representation for  $\bar{k} = \bar{0}$ .

Using the three basis functions in (6.65) leads to a dispersion relation which is of degree 3 in  $E$ , 6 in  $k_x$  and  $k_y$  and 3 in the strength of the "delta function" potential. If the potential is set equal to zero,

$$E = k_x^2 + k_y^2 \quad (6.66)$$

is one of the solutions.



At  $\bar{k} = \bar{0}$  the three roots for  $E(V = 0)$  are 0, 8.62, and 53.56. The value 8.62 is clearly not meaningful, and

$$53.56 \sim 16\pi^2/3 = 52.63787, \quad (6.67)$$

which is the second (first nonzero) energy for  $\bar{k} = \bar{0}$ . The reasonably good approximation to  $16\pi^2/3$  must be due to  $f_3$  being a properly restricted function.

If the strength of the delta function potential is set to unity, then the three roots  $E(0)$  are  $E = 1.94559$  (see Table VII),  $E = 15.5$  (as opposed to  $E = 8.62$  for  $V = 0$ ) and 53.59. If  $E$  is set equal to 8, the (lowest) curve of constant energy is very nearly given by

$$k_x^2 + k_y^2 = 8 - 1.94559 = 6.05441 \quad (6.68)$$

Typical points are

TABLE VIII

$k_x$	$k_y$	$k_x^2 + k_y^2$
$\pm 2.46057$	0	6.05441
$\pm 2.13129$	$\pm 1.23050$	6.05652
0	$\pm 2.46251$	6.06396

In the second row in Table VIII,  $\pm k_x = \sqrt{3}k_y$ , and so if the curve of constant energy had the symmetry of the lattice, then the two last entries in the column  $k_x^2 + k_y^2$  would be equal; this is evidently not the case for this approximation.

Let us now consider the method of restricted basis functions, first using trigonometric functions. For  $\bar{k} = \bar{0}$  and the identity representation we must insist that the functions be invariant under all of the operations which leave the





hexagon invariant, and that the normal derivative of the functions vanish at the edge of the Wigner-Seitz cell. For the trigonometric functions, the boundary conditions are automatically satisfied once the symmetry conditions are applied. The functions are linear combinations of the basis functions given by equation (6.55), that is, of expressions of the form (6.53). Typical basis functions used were:

$$\begin{aligned}
 f_1 &= 2 \\
 f_2 &= 2(2/3)^{1/2} \left[ \cos 2\pi \left( \frac{x}{\sqrt{3}} + y \right) + \cos 2\pi \left( \frac{x}{\sqrt{3}} - y \right) \right. \\
 &\quad \left. + \cos \frac{4\pi x}{\sqrt{3}} \right] \\
 f_5 &= 2(1/3)^{1/2} \left[ \cos 2\pi \left( \frac{x}{\sqrt{3}} + 3y \right) + \cos 2\pi \left( \frac{x}{\sqrt{3}} - 3y \right) \right. \\
 &\quad + \cos 4\pi \left( \frac{2x}{\sqrt{3}} + y \right) + \cos 4\pi \left( \frac{2x}{\sqrt{3}} - y \right) \\
 &\quad \left. + \cos 2\pi \left( \frac{5x}{\sqrt{3}} + y \right) + \cos 2\pi \left( \frac{5x}{\sqrt{3}} - y \right) \right] \quad (6.69)
 \end{aligned}$$

In general, six terms of the form (6.53) are required, but these are not necessarily distinct.

The matrices  $H = -L + V$  and  $N$  were evaluated for  $n = 1, 2, \dots, 6$ , and the eigenvalues in Table IX calculated.

TABLE IX

	n=1	n=2	n=3	n=4	n=5	n=6
E <sub>1</sub>	2.00000	1.91562	1.89980	1.89482	1.88492	1.88486
E <sub>2</sub>	--	50.62943	50.58870	50.58520	50.57090	50.57075
E <sub>3</sub>	--	--	153.97021	153.88063	153.85906	153.83866
E <sub>4</sub>	--	--	--	206.69606	206.69429	206.65892
E <sub>5</sub>	--	--	--	--	366.24924	366.24327
E <sub>6</sub>	--	--	--	--	--	470.46948



The higher roots are probably quite good since for large values of  $E$ , the problem approximates an empty lattice, and the basis functions used are empty lattice eigenfunctions.

We now consider the method of restricted basis functions, this time using polynomials to construct the basis functions. Again we treat the case  $\bar{k} = \bar{0}$  and the identity representation. We are looking, then, for polynomials which are invariant under all of the operations of the group of the hexagon, and which have in addition the property that their normal derivatives vanish on the edge of the hexagon.

The two polynomials

$$p = r^2 = x^2 + y^2 \quad (6.70)$$

and

$$Q = r^6 \cos 6\theta = x^6 - 15x^4y^2 + 15x^2y^4 - y^6 \quad (6.71)$$

already satisfy the hexagonal symmetry conditions. The functions

$$f_1 = 1$$

$$f_2 = 6p - 15p^2 + 10p^3 + 2Q$$

$$f_3 = p - 7p^3 + 7p^4 + 2pQ$$

$$f_4 = 5p^2 - 10p^3 - 15p^4 + 26p^5 + 10p^2Q \quad (6.72)$$

satisfy both the symmetry and boundary conditions. We note here that  $f_2$  in (6.72) above is identical to  $f_3$  of equation (6.65). The matrices  $N$  and  $H = -L + V$  were calculated, and the energies calculated for  $n = 1, 2, 3$ , and  $4$ .





TABLE X

	n=1	n=2	n=3	n=4
$E_1$	1.95358	1.91543	1.89157	1.88682
$E_2$	--	55.23205	54.74699	54.74006
$E_3$	--	--	187.40751	187.34800
$E_4$	--	--	--	236.69607

The lowest root  $E_1$  must be greater than the true value since a variational procedure was used, and the polynomial result 1.88682 at  $n = 4$  is better than the trigonometric result 1.89482, also at  $n = 4$ . The roots  $E_2$  and  $E_3$  from Table IX should be much better than the corresponding roots in Table X, and the apparent convergence of these roots in Table X must be due to very small components in the third and fourth polynomials of the second and third eigenfunctions of the problem.

Let us now consider the plane hexagon with a potential which is perhaps a better two dimensional analogue of a real crystal. The potential used was

$$V(\bar{r}) = \sum_i \frac{e^{-4|\bar{r}-\bar{r}_i|}}{|\bar{r}-\bar{r}_i|} \quad (6.74)$$

The "4" in the exponent was chosen to make the potential at the edge of a cell approximately 1/10 of the potential half way from the center to the edge of a cell. Only nearest neighbours were used without, then, introducing any serious errors.

The polynomials for  $\bar{k} = 0$  for the identity representation given in (6.73) were used as basis functions. The





necessary integrals were evaluated numerically using a Gaussian technique and are accurate to five figures. The energies found are given in the following table.

TABLE XI

	1	2	3	4
$E_1$	-1.80584	-1.89283	-1.91442	-1.91717
$E_2$	--	+48.11555	+47.48769	+47.46620
$E_3$	--	--	+180.60796	+179.75436
$E_4$	--	--	--	+357.67424

### The Face Centered Cubic Lattice

In choosing a physically interesting application the cubic lattices, having the highest symmetry among the space lattices, are clearly the logical choices. Of the three cubic lattices, the simple cubic is discarded since no materials are known which have this structure. The Wigner-Seitz cell for the body centered cubic lattice has two types of faces: squares and hexagons, and for this reason is somewhat more difficult an application than the face centered cubic lattice for which all faces of the Wigner-Seitz cell are equivalent rhombuses.

Since monovalent metals have relatively simple band structures compared with divalent metals, and because of the attention devoted to copper in the literature, it was decided to apply some of the new methods to copper. (See, for example, Howarth (1953), Fukuchi (1956), Segall (1961), Burdick (1961).)



The pioneer work of Seitz (1936) and Bouckaert, Smoluchowski and Wigner (1936) on the symmetry properties of electronic wave functions in crystals allows us to find linear combinations of powers of  $x$ ,  $y$  and  $z$  having the symmetries appropriate to any value of the wave vector  $\bar{k}$ . Knowing the group of operations under which a given  $\bar{k}$  is either invariant or transforms into an equivalent  $\bar{k}$ , and applying the Bloch boundary conditions results usually in a more stringent set of boundary conditions. For copper, a face centered cubic crystal, the irreducible representations corresponding to physically interesting energy values (Segall (1961)) for the three most symmetric points of the Brillouin zone are listed in Table XII. The corresponding symmetrized polynomials are also listed; these correspond to the lattice harmonics of Von der Lage and Bethe (1947) and Bell (1954). Finally, for the usual Wigner-Seitz unit cell bounded by the planes

$$\begin{aligned}\pm x \pm y &= a/2, \\ \pm y \pm z &= a/2, \\ \pm z \pm x &= a/2,\end{aligned}\tag{6.75}$$

are listed the boundary conditions which a wave function  $\psi$ , of the Bloch form, must satisfy. The boundary conditions are those of Howarth (1953) with some additions, and the error for  $X_5$  has been corrected. The notation used is that of Jones (1960), and of Bouckaert, Smoluchowski and Wigner (1936). We note that since the original problem is Hermitian, the diverse, more stringent boundary conditions which result from the application of the symmetry conditions do result in the



TABLE XII

$\bar{k}$	Irreducible Group Representation	Typical Symmetrized Polynomial	Boundary Conditions For First Polynomial Listed	Boundary
$\Gamma=(0,0,0)$	$O_h$	$x^4+y^4+z^4$	1. $\partial\psi/\partial n=0$	on $x+y=a/2$ (all faces equivalent)
	$\Gamma_{125}$ (triply degenerate)	$xyz^2$ $yzx^2$ $zxy^2$	1. $\partial\psi/\partial n=0$ 2. $\psi$ antisymmetric and $\partial\psi/\partial n$ symmetric	on $x+y=a/2$ about $z=x$ on $z+x=a/2$
	$\Gamma_{12}$ (doubly degenerate)	$x^2-y^2$ $z^2-(1/2)(x^2+y^2)$	1. $\psi=0$ 2. $\psi$ symmetric and $\partial\psi/\partial n$ antisymmetric	on $x+y=a/2$ about $z=x$ on $z+x=a/2$
$X=(0,0,2\pi/a)$	$D_{4h}$	$z^2(x^2+y^2)$	1. $\partial\psi/\partial n=0$ 2. $\psi$ antisymmetric and $\partial\psi/\partial n$ symmetric	on $x+y=a/2$ about $z=x$ on $z+x=a/2$
	$X_2$	$z^2(x^2-y^2)$	1. $\psi=0$ 2. $\psi$ antisymmetric and $\partial\psi/\partial n$ symmetric	on $x+y=a/2$ about $z=x$ on $z+x=a/2$
	$X_3$	$xyz^2$	1. $\partial\psi/\partial n=0$ 2. $\psi$ symmetric and $\partial\psi/\partial n$ antisymmetric	on $x+y=a/2$ about $z=x$ on $z+x=a/2$





TABLE XII (continued)

$X_5$ (doublet degenerate)	$3x^2y^2$ $xy^3z$	1. $\psi$ antisymmetric and $\partial\psi/\partial n$ symmetric	about $x=y$ on $x+y=a/2$
		2. $\psi$ symmetric and $\partial\psi/\partial n$ antisymmetric	about $y=z$ on $y+z=a/2$
		3. $\psi$ antisymmetric and $\partial\psi/\partial n$ symmetric	about $z=x$ on $z+x=a/2$
$X_4^1$	$z(x^2+y^2)$	1. $\partial\psi/\partial n=0$	on $x+y=a/2$
		2. $\psi$ symmetric and $\partial\psi/\partial n$ antisymmetric	about $z=x$ on $z+x=a/2$
$L_1$	$xy+yz+zx$	1. $\psi$ antisymmetric and $\partial\psi/\partial n$ symmetric	about $z=0$ on $x+y=a/2$
		2. $\partial\psi/\partial n=0$	on $x-y=a/2$
	$(x^2-y^2)$ $z^2-(1/2)(x^2+y^2)$	1. $\partial\psi/\partial n=0$	on $x+y=a/2$ on $x-y=a/2$
		2. $\psi=0$	about $z=x$ on $z+x=a/2$
$L_3$ (doubly degenerate)	$x+y+z$	3. $\psi$ antisymmetric and $\partial\psi/\partial n$ symmetric	about $z=-x$ on $z-x=a/2$
		4. $\psi$ symmetric and $\partial\psi/\partial n$ antisymmetric	about $z=-x$ on $z-x=a/2$
$L_2^1$	$x+y+z$	1. $\psi$ symmetric and $\partial\psi/\partial n$ antisymmetric	about $z=0$ on $x+y=a/2$
		2. $\partial\psi/\partial n=0$	on $x-y=a/2$





vanishing of the necessary surface integrals to allow the use of the variational procedure.

A start has been made in applying the method of restricted basis functions to this problem. For  $\bar{k} = \bar{0}$  and the identity representation, no polynomials exist of degree less than 12 (apart from a constant) which satisfy all of the conditions. By taking appropriately symmetrized linear combinations of terms like  $x^i y^j z^k$  of degree up to and including 12, the application of the boundary conditions resulted in 22 homogeneous linear equations in 21 unknowns. The equations were solved on the LGP-30 at the University of Alberta Computing Center using an excellent program written by Mr. A. Cseuz, and modified by Mr. D. L. Hunter. The coefficients  $A_{ijk}$  in Table XIII are the solutions to these equations, and are the coefficients of  $S_{ijk}$ , where

$$\begin{aligned}
 S_{ijk} &= x^i(y^j z^k + z^j y^k) + y^i(x^j z^k + z^j x^k) \\
 &\quad + z^i(x^j y^k + y^j x^k), \quad i \neq j \neq k \\
 S_{iij} &= x^i y^i z^j + y^i z^i x^j + z^i x^i y^j, \quad i \neq j \\
 S_{iii} &= x^i y^i z^i.
 \end{aligned} \tag{6.76}$$

Using symmetrized polynomials up to and including degree 14 resulted in 28 homogeneous equations in 30 unknowns. One solution to these equations will, of course, be the degree 12 polynomial already found. As yet the equations have not been solved, since the capacity of the LGP-30 has been exceeded. It was found that conventional floating point arithmetic methods



TABLE XIII

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$A_{2,0,0}$	=	-1,756,016,640
$A_{2,2,0}$	=	2,004,355,584
$A_{4,0,0}$	=	399,877,632
$A_{6,0,0}$	=	-43,464,960
$A_{4,2,0}$	=	-381,870,720
$A_{2,2,2}$	=	-2,347,107,840
$A_{8,0,0}$	=	3,204,432
$A_{6,2,0}$	=	24,992,352
$A_{4,4,0}$	=	68,690,160
$A_{4,2,2}$	=	409,812,480
$A_{10,0,0}$	=	-155,232
$A_{8,2,0}$	=	-582,120
$A_{6,4,0}$	=	-3,880,800
$A_{6,2,2}$	=	-23,284,800
$A_{4,4,2}$	=	-57,047,760
$A_{12,0,0}$	=	3,528
$A_{10,2,0}$	=	0
$A_{8,4,0}$	=	72,765
$A_{8,2,2}$	=	436,590
$A_{6,6,0}$	=	126,126
$A_{6,4,2}$	=	1,891,890
$A_{4,4,4}$	=	2,401,245

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resulted in far too little accuracy, and the program used does only integer arithmetic and gives exact answers. The  $28 \times 30$  set of equations results in large enough numbers to cause overflow when single precision arithmetic is used, and the memory of the machine is exceeded when one attempts to use double precision arithmetic.

As can be seen from Table XII the determination of restricted polynomials, except for those corresponding to  $\bar{k} = \bar{0}$  and the identity representation, requires the satisfaction of boundary conditions on at least two nonequivalent faces. At least one of these boundary conditions always turns out to involve the simultaneous symmetry of  $\psi$  and the antisymmetry of  $\partial\psi/\partial n$ , or vice versa, about a line of symmetry on the face of the Wigner-Seitz cell. This situation results in a very large number of simultaneous equations. Sets of such equations for several of the irreducible representations listed have been found. As in the case of the  $\Gamma_1$  polynomials, overflow was eventually encountered before complete solutions were obtained. It was found, however, that there was a considerable amount of linear dependence among the sets of equations.

We hope to solve all of these sets of equations when the magnetic tape units currently being installed are fully integrated into the IBM 1620 system at the Computing Center.

Another approach to the problem of constructing polynomial basis functions is to choose for the application of the boundary conditions, instead of the usual Wigner-Seitz rhombohedral dodecahedron, a cube of four times the volume bounded by the faces  $x = \pm a/2$ ,  $y = \pm a/2$ ,  $z = \pm a/2$ . Then at least for all of the irreducible representations listed in Table XII, the boundary conditions are the simple ones  $\psi = 0$







or  $\partial\psi/\partial n = 0$ . In compensation the cubic cell would contain not only the ion at the center of the cell, but also an ion at the midpoint of each edge.

By using the restricted basis functions consisting of both polynomials and trigonometric functions, we should be able to determine whether or not the polynomials are more suitable than the trigonometric basis, as was originally thought probable when the investigation began. And by using the resulting values of  $E(\bar{k})$  for the centers of all faces in the first Brillouin zone, the determinant interpolation procedure will provide a properly symmetrized dispersion relation.

Another possible interpolation procedure consists of fitting the special values of  $E(\bar{k})$  to a linear combination of polynomials in  $\bar{k}$ , each having complete cubic symmetry and vanishing normal derivative on the surface of the Brillouin zone.

Some of the above approaches may warrant further investigation.



## CHAPTER VII

SUMMARY AND CONCLUSIONS

The new methods developed in Chapter V seem to have some advantages over the standard methods presented in Chapter IV. The standard cellular methods all make spherical approximations, either to the potential inside part of the Wigner-Seitz cell, or to the unit cell itself, or both. The new methods obviate such spherical approximations which, in some cases at least, may result in relatively large inaccuracies. The Tight Binding and Orthogonalized Atomic Orbitals methods are essentially variational or equivalent matrix approaches with particular choices for the basis functions: atomic orbitals or linear combinations of atomic orbitals chosen to make the overlap integrals vanish. These choices of basis functions may not always be realistic.

The plane wave method, also a variational method, has the obvious difficulty of apparent convergence to a valence state, followed eventually by convergence to the innermost core state, if the potential used does not take into account the tightly bound core electrons. The orthogonalized plane wave method developed by Herring (1940) does not really overcome the difficulty, it merely postpones it. If the core states to which the plane waves are made orthogonal were exactly eigenfunctions of the Hamiltonian, then the variational procedure would indeed converge to the lowest valence state. Since the core states available are only approximations to the lower eigenfunctions of the Hamiltonian, then orthogonalizing the basis functions to these core states provides one with a set of basis functions all with relatively small, but nonzero,



components of the lower eigenfunctions of the Hamiltonian being used. The variational procedure, then, will still eventually provide the innermost core electron energy, but many basis functions will be required before this occurs. The convergence in the energy to a valence state with only a few basis functions is still only an apparent convergence, a "plateau" in the decrease of the lowest eigenvalue with increasing  $n$ , the number of basis functions. The difference between this plateau and the first valence state of the Hamiltonian depends, of course, on the core states used in the orthogonalization procedure and the exact core states of the Hamiltonian under consideration. As the core states being used approach the true core states, the difference between the plateau in the eigenvalue versus  $n$  curve and the first valence state will decrease, and at the same time the plateau will lengthen and become an asymptote as  $n \rightarrow \infty$ .

For a given set of approximate core wave functions, there is, of course, a "best"  $n$ , for which the lowest eigenvalue will most closely approximate the first valence state, but attempting to determine this best  $n$  would not appear to be a fruitful approach. Since the states favored by the variational procedure depend only on the basis functions used, in principle one could find the first valence state, say the  $m$ 'th state, by using basis functions containing significant components of all of the first  $n$  states,  $n > m$ . One would then use the variational procedure, and pick the  $m$ 'th lowest eigenvalue; the first  $n$  atomic orbitals might serve nicely as such basis functions. The matrices involved, of course, would be fairly large, with corresponding computational difficulties.







Another method of achieving the first valence state is by the use of a pseudopotential (Calloway (1958)) which does take into account the core electrons. This procedure would involve considerably less labour, but the accuracy of the resulting eigenvalues would, of course, depend on the accuracy of the pseudopotential.

The three new methods developed in Chapter V appear to have some advantages over the standard procedures. The restricted basis functions, once found, may be used for the same lattice structure with a variety of potentials. The convergence of the lowest state is fairly rapid in the cases considered in Chapter VI, whether the basis functions are trigonometric or polynomial, and one cannot on this evidence choose between them. The trigonometric basis functions are certainly easier to find, though it may be that for a real crystal one set of basis functions may be significantly better than the other for rapidity of convergence.

The consistency determinant provides a straightforward procedure for obtaining an approximation to the entire dispersion relation. The relation obtained, however, is implicit, and it is possible that an inordinate number of basis functions would have to be used to obtain sufficient accuracy. Better results for the lowest eigenvalue for the plane hexagon at  $k = 0$  were obtained with two restricted polynomials (1.91543) and with two restricted trigonometric functions (1.91562), than with seven basis functions for the consistency determinant (1.92219). (The best answer obtained was with six trigonometric functions: 1.88486) It seems unlikely that the correct energy is less than 1.863, in which case the result from the consistency determinant is in error by less than 2.1%, and one could find the entire lowest sheet of  $E = E(k)$ , with much the same accuracy.



From the evidence in Tables IV, V and VI, the consistency determinant used as an interpolation aid appears very encouraging. Together with the method of restricted basis functions for finding values of  $E(\bar{k})$  at symmetry points in the first Brillouin zone, the consistency determinant may prove useful.



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